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Eastern Lake Survey
(Phase 1 - Synoptic Chemistry)
Quality Assurance Report

Lockheed Engineering and Management
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NATIONAL SURFACE WATER SURVEY
EASTERN LAKE SURVEY (PHASE I -- SYNOPTIC CHEMISTRY)
QUALITY ASSURANCE REPORT

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This report provides an overview of the quality assurance activities and results of the Eastern Lake Survey - Phase I. The quality assurance program used a combination of blank, duplicate, and audit samples to provide an external check on the data quality of 32 physiochemical parameters measured and to allow early detection of problems in sample collection, processing, and analysis. Field sampling, field and analytical laboratory, and database quality control protocols also were standardized to ensure the reliability of the data.

The survey results were verified to identify and to correct, qualify, or eliminate data of unacceptable quality. The verification process was based on known relationships between the physiochemical parameters. The quality of the data for 10 nonchemical parameters also was determined during the validation process. A final data set, which was generated from the validated data, was used for calculating population estimates.

The statistical analysis of the verified data set included estimates of instrumental and system detection limits, system decision limits, overall and analytical within-batch precision, and overall and analytical among-batch precision. Quantitation limits also were calculated for use in evaluating the precision of the survey data. The results of these statistical analyses were compared to the data quality objectives for detectability and for precision.

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PREFACE

The National Surface Water Survey (NSWS) is a three-phase project of the National Acid Precipitation Assessment Program (NAPAP). The objectives of the survey are to evaluate the current water chemistry of acid-sensitive lakes and streams in the U.S., to determine the status of fisheries and other biotic resources in those waters, and to quantify changes in a representative subset of lakes and streams through a long-term monitoring program. Phase I of the Eastern Lake Survey is the first part of the NSWS lake study.

This report is a supporting document to the Eastern Lake Survey - Phase I final report (Linthurst et al. 1986). This report is a companion document to the Eastern Lake Survey - Phase I quality assurance plan (Drousé et al. 1986), analytical methods manual (Hillman et al. 1986), and field operations report (Morris et al. 1986).

ABSTRACT

This report provides an overview of the quality assurance activities and results of the Eastern Lake Survey - Phase I, which evaluated the chemical status of 1,798 lakes in the eastern United States.

The quality assurance program used a combination of blank, duplicate, and audit samples to provide an external check on the data quality of 32 physicochemical parameters measured and to allow early detection of problems in sample collection, processing, and analysis. Field sampling, field and analytical laboratory, and data base quality control protocols also were standardized to ensure the reliability of the data.

The survey results were verified to identify and to correct, qualify, or eliminate data of unacceptable quality. The verification process was based on known relationships between the physicochemical parameters. The verified data were validated by using exploratory procedures to identify outliers and systematic differences; these discrepancies indicated possible errors in the chemical analyses that could not be revealed by the verification process. The quality of the data for 10 nonchemical parameters also was determined during the validation process. A final data set, which was generated from the validated data, was used for calculating population estimates.

The statistical analysis of the verified data set included estimates of instrumental and system detection limits, system decision limits, overall and analytical within-batch precision, and overall and analytical among-batch precision. Quantitation limits also were calculated for use in evaluating the precision of the survey data. The results of these statistical analyses were compared to the data quality objectives for detectability and for precision. An additional statistical evaluation of the survey data, including a discussion of accuracy determinations, is appended to this report.

Overall, Phase I of the Eastern Lake Survey was successful in achieving its objectives. The quality assurance requirements proved adequate to ensure that all samples were collected and analyzed consistently, and that the quality of the resulting data was known.

This report covers a planning, implementation, and data review period from March 1983 to January 1986, and work was completed as of December 1986.

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SECTION 1

INTRODUCTION

The National Surface Water Survey (NSWS) is a three-phase project within the National Acid Precipitation Assessment Program (NAPAP). The NSWS was initiated by the U.S. Environmental Protection Agency (EPA) in 1983. The purpose of Phase I of the NSWS is to document the present chemical status of lakes and streams in areas of the U.S. that are potentially susceptible to the effects of acidic deposition (Linthurst et al. 1986). Phase II of the survey is intended to determine the present status of biotic resources and to assess the chemical variability within and among surface waters characterized during Phase I. Phase III, a long-term monitoring program, will quantify changes in the aquatic resources of a subset of Phase II surface waters.

EASTERN LAKE SURVEY - PHASE I

This report summarizes the results of the QA program for Phase I of the Eastern Lake Survey (ELS-I). The QA program, including data verification and validation procedures, is discussed in greater detail in Drousé et al. (1986). Analytical methods and field sampling protocols for the ELS-I are discussed in detail in Hillman et al. (1986) and Morris et al. (1986), respectively. The statistical design for lake sampling is described in Linthurst et al. (1986). In total, 1,798 lakes were sampled in the ELS-I. The lakes were selected from three regions east of the Mississippi River that are potentially susceptible to acidification (Figure 1).

SURVEY PARTICIPANTS

Planning, conducting, and interpreting a study of the magnitude of the NSWS required the cooperation of numerous government agencies and private organizations. Development of the NSWS included definition of measurement requirements and survey objectives, which was accomplished through discussions at meetings and workshops. Participants included representatives of several government agencies as well as other scientists involved in acidic deposition research.

The U.S. EPA Environmental Monitoring Systems Laboratory-Las Vegas, Nevada (EMSL-LV) had primary responsibility for the ELS-I QA program and sampling operations. Much of the technical effort in this area was provided by Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO) which is the prime contractor for EMSL-LV. The relevant state agencies and EPA regional offices were also involved in the sampling activities. The data base operations were performed by Oak Ridge National Laboratory (ORNL). The EPA Environmental Research Laboratory-Corvallis, Oregon (ERL-Corvallis) had primary responsibility for design and planning of the ELS-I, as well as for data validation and interpretation.

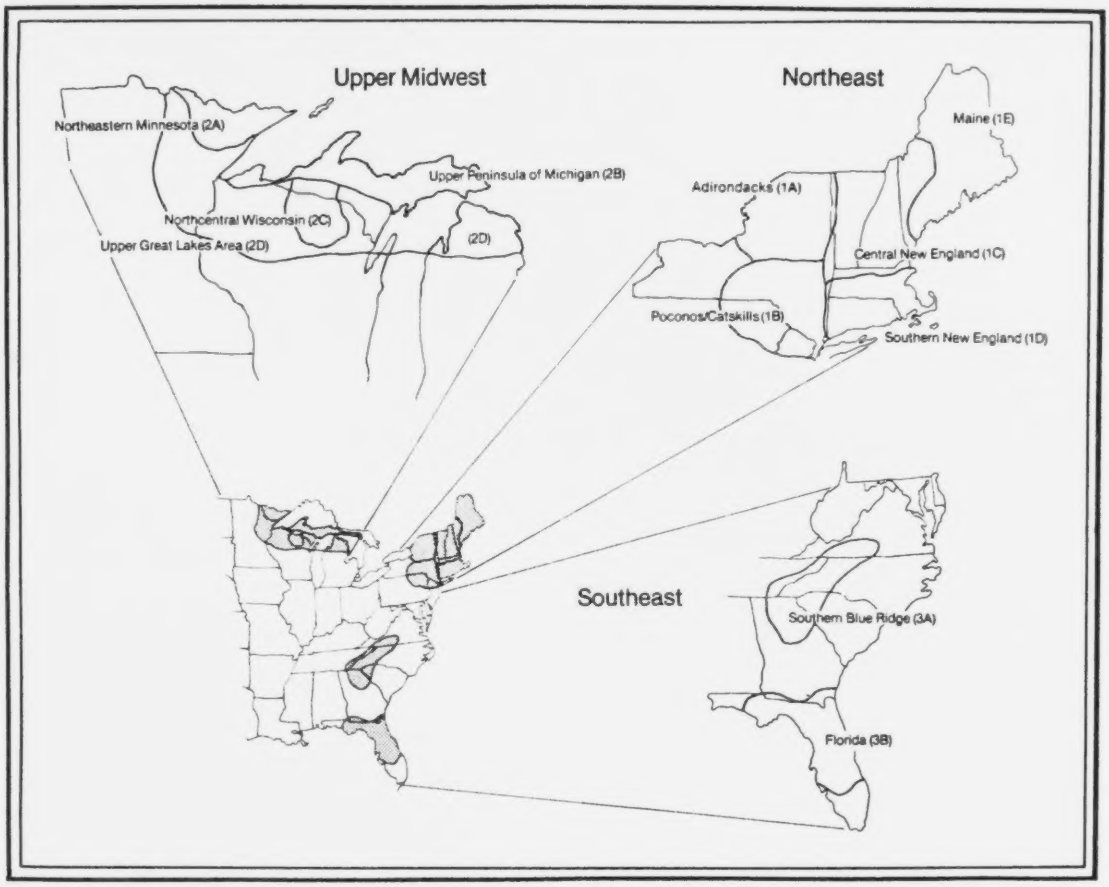

Upper Midwest
Northeast
Northeastern Minnesota (2A)
Upper Peninsula of Michigan (2B)
Northcentral Wisconsin (2C)
Upper Great Lakes Area (2D)
(2D)
Maine (1E)
Adirondacks (1A)
Central New England (1C)
Poconos/Catskills (1B)
Southern New England (1D)
Southeast
Southern Blue Ridge (3A)
Florida (3B)

Figure 1. Regions and subregions sampled during the Eastern Lake Survey - Phase I (from Linthurst et al. 1986).

MEASUREMENT REQUIREMENTS

The first step in design of the QA program was to define the measurement requirements for the ELS-I. Thirty-two parameters were selected for in situ or laboratory measurement during Phase I (Table 1). The EPA data users (see Linthurst et al. 1986) reasoned that measurement of these chemical and physical parameters would provide adequate information from single lake samples for the evaluation of the present status of lakes and thus would meet the objectives of Phase I. A description of each parameter is presented in Overton et al. (1986) and in Kanciruk et al. (1986).

DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for precision, accuracy, representativeness, comparability, and completeness were defined early in 1984. The anticipated range of measurement values for each parameter and the required detection limits were also specified for each measurement. Precision is the repeatability of a measurement and accuracy is the closeness of a measured value to the true value. Representativeness is the degree to which the sample data characterize the population of interest and is a function of the sampling of the sampling design (see Linthurst et al. 1986). Comparability is the level of confidence with which two or more data sets are similar in precision, accuracy, and representativeness, and completeness is the proportion of valid data obtained from a measurement system.

The DQOs were developed using data from published literature. Equipment, sampling protocols, and analytical methodologies were selected and standardized in order to achieve the DQOs. Pilot studies were implemented to evaluate and revise the methodologies, equipment, and DQOs. One change in the DQOs that resulted from the pilot study was in the detection limit for total phosphorus which was lowered from 0.003 to 0.002 mg L^{-1}. The final DQOs were provided in a document delivered to the quality assurance management staff of the EPA in October 1984. The observed ranges of values in the verified data set, the required detection limits, the precision and accuracy goals, the maximum sample holding times, and the measurement methods used for each parameter are listed in Table 1. The instances where extreme values affected the estimated precision are listed in Section 5.

DEVELOPMENT OF DOCUMENTS FOR THE EASTERN LAKE SURVEY - PHASE I

Protocols for sampling, chemical analysis, and data processing were based on the best available published methods. A draft QA plan and a draft analytical methods manual were used during the pilot studies. Prior to commencement of the ELS-I, the draft QA plan and the draft analytical methods manual were revised on the basis of results obtained from the pilot studies. The final QA plan and the final methods manual incorporated those revisions and any changes implemented during the ELS-I.

PILOT STUDIES

Two pilot studies for the ELS-I were undertaken during the winter and spring of 1984. The winter pilot study was conducted in January 1984 and

TABLE 1. PARAMETERS MEASURED, QUALITY ASSURANCE CRITERIA, AND ANALYTICAL METHODS FOR THE EASTERN LAKE SURVEY - PHASE I

Parameter[a]	Observed Range	Required Detection Limit	Intra-Laboratory Precision (Maximum % RSD)[b]	Accuracy (Maximum % Absolute bias)	Maximum Sample Holding Time - Days (Analytical Lab)	Instrument or Method[c]	Reference (Laboratory Methods)[d]
IN SITU							
pH	3.60 - 10.46	--	--	0.1[e]	--	Potentiometer (Hydrolab)	Morris et al. (1986)
Conductance, μS cm^{-1}	0.0 - 1267.0	--	--	--	--	Conductivity cell (Hydrolab)	Morris et al (1986)
Lake temperature, °C	--	--	--	--	--	Thermistor (Hydrolab)	Morris et al. (1986)
Secchi disk transparency, m	--	--	--	--	--	Secchi disk	Morris et al. (1986)
FIELD LABORATORY							
Laboratory pH (closed system)	3.81 - 9.36	--	0.1[e]	0.1[e]	--	pH meter Orion Model 611	EPA 150.1
Dissolved inorganic carbon (closed system), mg L^{-1}	0.16 - 48.99	0.05	10	10	--	Infrared spectroscopy Dohrmann DC-80 carbon analyzer	EPA 415.2 (modified)
True color, PCU	0 - 345	0	5[e]	--	--	Comparator Hach Model CO-1	EPA 110.2 (modified)
Turbidity, NTU	0 - 290	2	10	10	--	Nephelometer Monitek Model 21	EPA 180.1
CONTRACT ANALYTICAL LABORATORY							
Acid-neutralizing capacity (ANC), μeq L^{-1}	-209.1 +4046.6	--[h]	10	10	14	Acidimetric titration, modified Gran analysis	Hillman et al. (1986); Kramer (1984)
Aluminum (Al), mg L^{-1}(f)							
total extractable	-0.009 - 3.594	0.005	10 (>0.010) 20 (≤0.010)	10 (>0.010) 20 (≤0.010)	7	Furnace AAS on MIBK extract	Hillman et al. (1986)
total	-0.002 - 9.678	0.005	10 (>0.010) 20 (≤0.010)	10 (>0.010) 20 (≤0.010)	28	Furnace AAS	EPA 202.2

(continued)

TABLE 1. (continued)

Parameter[a]	Observed Range	Required Detection Limit	Intra-Laboratory Precision (Maximum % RSD)[b]	Accuracy (Maximum % Absolute bias)	Maximum Sample Holding Time - Days (Analytical Lab)	Instrument or Method[c]	Reference (Laboratory Methods)[d]
Ammonium (NH_4^+), mg L^{-1}(g)	-0.06 - 1.63	0.01	5	10	28	Colorimetry (phenate, automated)	EPA 350.1
Base-neutralizing capacity (BNC), µeq L^{-1}	--	--h	10	10	14	Alkalimetric titration, modified Gran analysis	Hillman et al. (1986); Kramer (1984)
Calcium (Ca), mg L^{-1}(g)	0.19 - 60.94	0.01	5	10	28	Flame AAS, ICPES	EPA 215.1
Chloride (Cl^-), mg L^{-1}(g)	0.01 - 94.70	0.01	5	10	28	IC	ASTM (1984a); O'Dell et al. (1984)
Conductance, µS cm^{-1}	7.8 - 3613.3	--i	1	5	14	Conductivity cell	EPA 120.1
Dissolved inorganic carbon (DIC) (air-equilibrated), mg L^{-1}	-0.07 - 46.91	0.05	10	10	14	IR	EPA 415.2 (modified)
Dissolved inorganic carbon (DIC) (initial ANC), mg L^{-1}	0.15 - 49.83	0.05	10	10	14	IR	EPA 415.2 (modified)
Dissolved organic carbon (DOC), mg L^{-1}	0.0 - 48.2	0.1	5 (>5.0) 10 (≤5.0)	10	14	IR	EPA 415.2
Fluoride (F^-), total dissolved, mg L^{-1}(g)	0.001 - 0.839	0.005	5	10	28	ISE	EPA 340.2 (modified)
Iron (Fe), mg L^{-1}(f)	-0.03 - 2.64	0.01	10	10	28	Flame AAS, ICPES	EPA 236
Magnesium (Mg), mg L^{-1}(g)	0.10 - 39.76	0.01	5	10	28	Flame AAS, ICPES	EPA 242.1
Manganese (Mn), mg L^{-1}(f)	-0.02 - 2.03	0.01	10	10	28	Flame AAS, ICPES	EPA 243.1

(continued)

TABLE 1. (continued)

Parameter[a]	Observed Range	Required Detection Limit	Intra-Laboratory Precision (Maximum % RSD)[b]	Accuracy (Maximum % Absolute bias)	Maximum Sample Holding Time - Days (Analytical Lab)	Instrument or Method[c]	Reference (Laboratory Methods)[d]
Nitrate (NO_3^-), mg L^{-1}(g)	-0.106 - 30.600	0.005	10	10	7	IC	ASTM (1984a); O'Dell et al. (1984)
pH (air-equilibrated)	3.82 - 8.93	--	0.05[e]	0.1[e]	7	pH meter	EPA 150.1
pH (initial ANC)	3.80 - 8.78	--	0.05[e]	0.1[e]	7	pH meter	EPA 150.1
pH (initial BNC)	3.81 - 8.82	--	0.05[e]	0.1[e]	7	pH meter	EPA 150.1
Phosphorus (P), total, mg L^{-1}(f)	-0.006 - 0.833	0.002	10 (>0.010) 20 (≤0.010)	10 (>0.010) 20 (≤0.010)	28	Colorimetry (phosphomolybdate or modification, automated)	USGS I-4600
Potassium (K), mg L^{-1}(g)	0.00 - 24.98	0.01	5	10	28	Flame AAS	EPA 258.1
Silica (SiO_2), mg L^{-1}(f)	-1.14 - 43.53	0.05	5	10	28	Colorimetry (automated)	USGS I-2700
Sodium (Na), mg L^{-1}(g)	0.06 - 323.00	0.01	5	10	28	Flame AAS	EPA 273.1
Sulfate (SO_4^{2-}), mg L^{-1}(g)	0.00 - 119.00	0.05	5	10	28	IC	ASTM (1984a); O'Dell et al. (1984)

[a] Dissolved ions and metals were determined, except where noted.

[b] Precision was estimated for samples at concentrations above 10 times instrumental detection limits, except where noted. %RSD = percent relative standard deviation.

[c] AAS = atomic absorption spectroscopy; MIBK = methyl isobutyl ketone; ICPES = inductively coupled plasma emission spectroscopy; IC = ion chromatography; IR = infrared spectrophotometry; ISE = ion-selective electrode.

[d] EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

[e] Absolute value in applicable units.

[f] Values converted to μg L^{-1} for data analysis. Required detection limits are in mg L^{-1}.

[g] Values converted to μeq L^{-1} for data analysis. Required detection limits are in mg L^{-1}.

[h] The absolute value of each laboratory calibration blank measurement was required to be less than 10 μeq L^{-1}.

[i] The mean of six nonconsecutive blank measurements was required to be less than 0.9 μS cm^{-1}.

consisted of sampling 50 ice-covered lakes in Maine, New Hampshire, and Vermont. During the spring pilot study in May-June, 137 lakes in Maine, New Hampshire, Vermont, Massachusetts, and New York were sampled. These studies were implemented to evaluate all aspects of the NSWS research plan including lake selection, proposed sampling protocols, the QA program, and data management. Objectives of the pilot studies are outlined in greater detail in Drousé et al. (1986). The process of lake selection is discussed in Linthurst et al. (1986).

SAMPLING AND ANALYTICAL METHODOLOGIES

Modifications to the original sampling and analytical protocols were made based on the experience gained during the pilot studies. These modifications included elimination of the dissolved oxygen measurements which were deemed to be time consuming and unnecessary, and revision of the sample-bottle washing procedure which had been introducing nitrate contamination (see Section 4). In addition, four experiments were conducted prior to the ELS-I to investigate (1) the possibility of contamination by helicopter exhaust, (2) representativeness of single-point sampling, (3) variability of measurements made using the Hydrolab units, and (4) effects of increased pressure (depth) on Hydrolab accuracy (Morris et al. 1986).

The primary objectives of base site operations were to obtain accurate physicochemical and geographical data at each lake site, to collect representative lake samples without introducing contamination, to preserve the integrity of samples until their analysis at contract laboratories, and to perform selected chemical analyses. The field laboratory operations are defined as follows:

- receive lake and QA samples and field data from each sampling team and assess sample condition upon receipt
- review lake data forms for accuracy and completeness
- incorporate audit samples with lake samples to form a batch of samples for analysis
- analyze the batch of samples for pH, DIC, true color, and turbidity
- perform aluminum extraction
- filter, preserve, and ship samples to contract analytical laboratories for detailed analysis
- coordinate sample shipment information with the Sample Management Office and EMSL-LV
- distribute copies of NSWS Forms 1 and 2 to the appropriate offices

The protocols for collection of field data and water samples during the ELS-I were implemented in three phases: preflight preparation, lake site activities (including sampling methodologies), and postflight operations (Morris et al. 1986).

Standardized forms were developed to record measurements made at each lake and at the field and contract analytical laboratories. The multicopy field and field laboratory forms were checked for completeness and internal consistency at the field station. One copy of each form was sent to Oak Ridge National Laboratory for entry into the NSWS data base, and a second copy was sent to quality assurance personnel in Las Vegas; both copies were sent by overnight mail service. Transfer of samples and data is discussed in Section 3.

Analytical methodologies were selected for the ELS-I on the basis of guidelines from the DQOs. For some analytes, two or more techniques were considered to be equivalent (Hillman et al. 1986) based on published literature. The pilot studies and field and laboratory experiments provided opportunities to evaluate the relative merits of each technique. Two techniques were judged to be equivalent for determining the concentrations of total phosphorus and of dissolved metals (Ca, Fe, K, Mg, Mn, Na), and either technique was permitted. However, measurements of free (uncomplexed) dissolved fluoride by ion-selective electrode and of total dissolved fluoride by ion chromatography were found to lack reproducibility, and these methods were eliminated. The field measurement and analytical methods used for the ELS-I are summarized in Table 1.

DATA COMPARABILITY STUDIES

Standardized techniques were specified for sampling and chemical analysis of water samples from the ELS-I. Standardization ensured that the effect (if any) of variance from sampling and analysis on the differences between lakes could be identified.

Studies were also undertaken to determine whether ELS-I data could be compared to survey data from other countries and to data obtained by using different analytical methods. Subsamples from 215 ELS-I samples collected in the southern Blue Ridge Mountains (NSWS subregion 3A, see Figure 1) were shipped via commercial courier to Norway for chemical analysis of 14 parameters. Similarly, 105 subsamples from the Adirondack Mountains (NSWS subregion 1A) were analyzed in Canada for 18 chemical parameters. Results of this study are summarized in Section 4 (Methods Evaluation) and are presented in greater detail in M. A. Stapanian et al. (in preparation).

A second study utilized 2047 split samples from the ELS-I to compare chemical analyses by flame atomic absorption spectroscopy (AAS) and inductively coupled plasma emission spectroscopy (ICPES). The ICPES analyses were performed at ERL-Corvallis and by ELS-I laboratories, and the flame AAS analyses were performed by ELS-I laboratories only. These analyses are presented in J. L. Engels et al. (in preparation).

SECTION 2

OPERATIONAL QUALITY ASSURANCE-QUALITY CONTROL PROGRAM

The QA plan (Drousé et al. 1986) describes the quality assurance-quality control (QA-QC) program of the ELS-I, and the analytical methods manual (Hillman et al. 1986) documents all methodologies used in the survey at the standard-operating-procedure (SOP) level of detail. The major aspects of the operational QA-QC program are summarized in the following sections. Quality assurance aspects related to the data base are discussed in Section 3. Field station organization and operations are described in Morris et al. (1986).

SELECTION OF ANALYTICAL LABORATORIES

The analytical requirements and QA approach were defined during the development of the QA program. The estimated number of samples to be analyzed and the estimated rate of sample collection were defined in the logistics planning. It was recognized early in the planning that no single analytical laboratory could analyze the number of expected samples at the rate they were to be collected and still meet the QA-QC requirements (especially the required holding times) that had been established. There was not a single EPA laboratory that had all of the analytical capabilities or resources to provide the required analytical support. This meant that the analytical support would have to be obtained via contracts with commercial analytical laboratories. A Contract Laboratory Program (CLP) had already been established to support the hazardous waste monitoring activities of the Environmental Protection Agency across the United States. Use of the CLP to obtain analytical laboratories for the NSWS was the most cost-effective approach. Use of multiple analytical laboratories also meant that additional care had to be taken in the selection and documentation of analytical methods and QA activities to ensure consistent and adequate performance in all laboratories. The contracting process required the following activities:

- preparation of a statement of work (SOW) that defined the analytical and QA-QC requirements in a contractual format

- preparation and advertisement of an invitation for bids (IFB) to solicit contractor support

- evaluation of the lowest bidders to assure that qualified laboratories were selected

Statement of Work

Control of data quality within each analytical laboratory was necessary in order to control data quality among the different laboratories and to minimize the data variability. The methods manual and QA plan had been drafted in the early phases of the planning process. However, in order to obtain analytical support contracts, the methods and the QA-QC requirements had to be prepared in a contractual format or statement of work (SOW). This involved careful review of the analytical and logistics requirements to assure that they were clearly stated and could be enforced under the terms of the contracts. Every effort was made to assure that the reporting and QC requirements were clearly stated in the SOW. The major contractual requirements in the SOW were the following:

- A contractor could bid on the analysis of one or more bid lots (500 samples per bid lot) that would be delivered to the analytical laboratory at a maximum rate of 30 samples per day per bid lot.

- Maximum holding times were specified. Failure to meet this requirement resulted in a penalty to the contractor of 20 percent per day per analytical subunit (7-, 14-, or 28-day holding time group) to a maximum of 100 percent of the bid price.

- Delivery of the completed data package was required within 35 days of sample receipt by the contractor. An incentive fee for early delivery of data and a penalty for late delivery of data (1 percent per day up to a maximum of 10 percent of the bid price in each case) were established.

- Failure of the contractor to provide adequate QA-QC data and deliverables as required by the SOW resulted in a penalty of up to 15 percent of the bid price.

The contractor laboratories were required to follow the methods exactly as specified in the SOW. The QA manager was allowed to make technical interpretations for the laboratory, but contractual changes were only made with the approval of the EPA contract officer.

Invitation for Bids

The SOW and IFB reflected the experience gained from using contract analytical laboratories during the pilot studies. The IFB was prepared and advertised in Commerce Business Daily. Approximately 200 laboratories responded to the advertisement and were sent copies of the SOW. Twenty-five laboratories submitted bids. The twelve lowest bidders were considered to have submitted reasonable bids and were selected to receive the preaward performance evaluation (PE) samples for the second step of the selection process.

Analytical Laboratory Evaluation

The lowest bidders were required to analyze PE samples and to report the results within 15 days after sample receipt. The PE samples were prepared to represent lake samples at both the low and high concentrations expected for the survey. Each bidder's data and data package were evaluated and scored. The scoring was based on evaluation of the quality of the analytical data as well as the quality and completeness of the data package itself. This process eliminated those laboratories that could not perform the analytical and data reporting requirements. A more detailed description of analytical laboratory performance evaluations is provided in Drousé et al. (1986).

Each of the laboratories that passed the PE sample evaluation was visited by an EPA team in order to verify the qualifications and capabilities of the laboratories to meet the contractual requirements. The EPA team determined whether the analytical laboratory had adequate equipment, personnel, and facilities to analyze samples in accordance with the SOW. These visits also provided an opportunity to clarify contract requirements with the analytical staff and to identify deficiencies that were observed in the PE sample data evaluation. The results of these on-site evaluations are on file with the QA manager. The lowest bidders who passed both the PE sample and on-site evaluations were awarded contracts to provide analytical services for the ELS-I.

TRAINING

Data quality depended on the ability of the field and laboratory personnel to properly collect, process, and analyze the samples. Operation of the ELS-I required a large staff composed of Lockheed-EMSCO employees, EPA regional and EMSL personnel, and the contract analytical laboratories. Training was essential to ensure consistent application of all operational and quality assurance procedures. Lockheed-EMSCO field sampling personnel received 6 days of intensive technical and safety training during a 15-day orientation program in September 1984 at the U.S. EPA EMSL-LV. Personnel from the regional EPA offices who would be involved in sampling were trained at the field stations prior to commencement of sampling. Details of these training sessions are contained in Morris et al. (1986).

A meeting was held in early August 1984 to review and discuss the objectives and requirements for the ELS-I. Participants included representatives from the NSWS management team, EMSL-LV QA staff, data base management team, contract analytical laboratories, and the analytical support laboratory. The objective of the meeting was to ensure that all parties would implement both the analytical methods and the QA and QC procedures accurately and consistently. This meeting also provided an opportunity for the participants to clarify the survey requirements.

COMMUNICATIONS

Coordination of the ELS-I operations required close communication to ensure that all program objectives were met. During the actual sampling phase, the most critical lines of communication were between Las Vegas and the field stations and between Las Vegas and the contract analytical laboratories. Daily communication was required concerning both logistical and quality assurance topics. Field sampling activities were closely monitored each day to ensure safety and logistical coordination. Logistics personnel in Las Vegas also coordinated and tracked the shipment of samples to the analytical laboratories and coordinated the shipment of supplies to field stations. Field communications are discussed in greater detail in Morris et al. (1986).

Daily calls also were made to each contract analytical laboratory by the Las Vegas QA staff. The primary objective of these calls was to ensure that the QA and QC procedures were being implemented according to the survey requirements and that the samples were being handled and analyzed properly. Other technical and logistical issues were addressed as they arose. Examples of issues that were quickly identified or resolved as a result of these calls include:

- aluminum contamination in aliquot 7 during the digestion step of the analysis for total aluminum
- incorrect calculations for reporting nitrate and silica data
- sample overload at one laboratory
- nitrate contamination in aliquot 3
- illegible data reporting

The daily QA contact with each laboratory continued until sample analysis was completed. Preliminary sample data were obtained either verbally, via computer, or via TELEFAX. The preliminary data were evaluated by comparing QA sample values with preliminary acceptance criteria which were calculated from pilot study data or from early QA sample data obtained early in the survey.

SAMPLING AND FIELD LABORATORY QUALITY CONTROL PROTOCOLS

The ELS-I incorporated a number of QC procedures into the sampling and analytical activities. The field sampling QC procedures included daily calibration of the Hydrolab unit, measurements of QCCS for pH and conductance, and sampling site verification. The field laboratory QC procedures included measurements of QCCS and a field laboratory (trailer) duplicate for DIC, pH, turbidity, and true color with each batch of samples. Samples also were preserved and were prepared for shipment to analytical laboratories for additional chemical analyses as part of the QC requirements. Specific QC procedures are outlined in Drousé et al. (1986), Hillman et al. (1986), and Morris et al. (1986). The flow of samples and data from the field sites through the field laboratories and the analytical laboratories is illustrated in Figure 2.

Sample Preservation

For each chemical parameter measured during the ELS-I, it was necessary to identify the procedures required for sample preservation. The objectives of sample preservation were to (1) inhibit chemical and biological activity, (2) prevent changes which are due to volatilization, and (3) prevent precipitation or adsorption effects. These considerations led to a sample preparation process in the field laboratory in which seven preserved aliquots were prepared from each bulk (routine, field duplicate, field blank, or field audit) sample. The preservation process used for each aliquot is listed in Table 2.

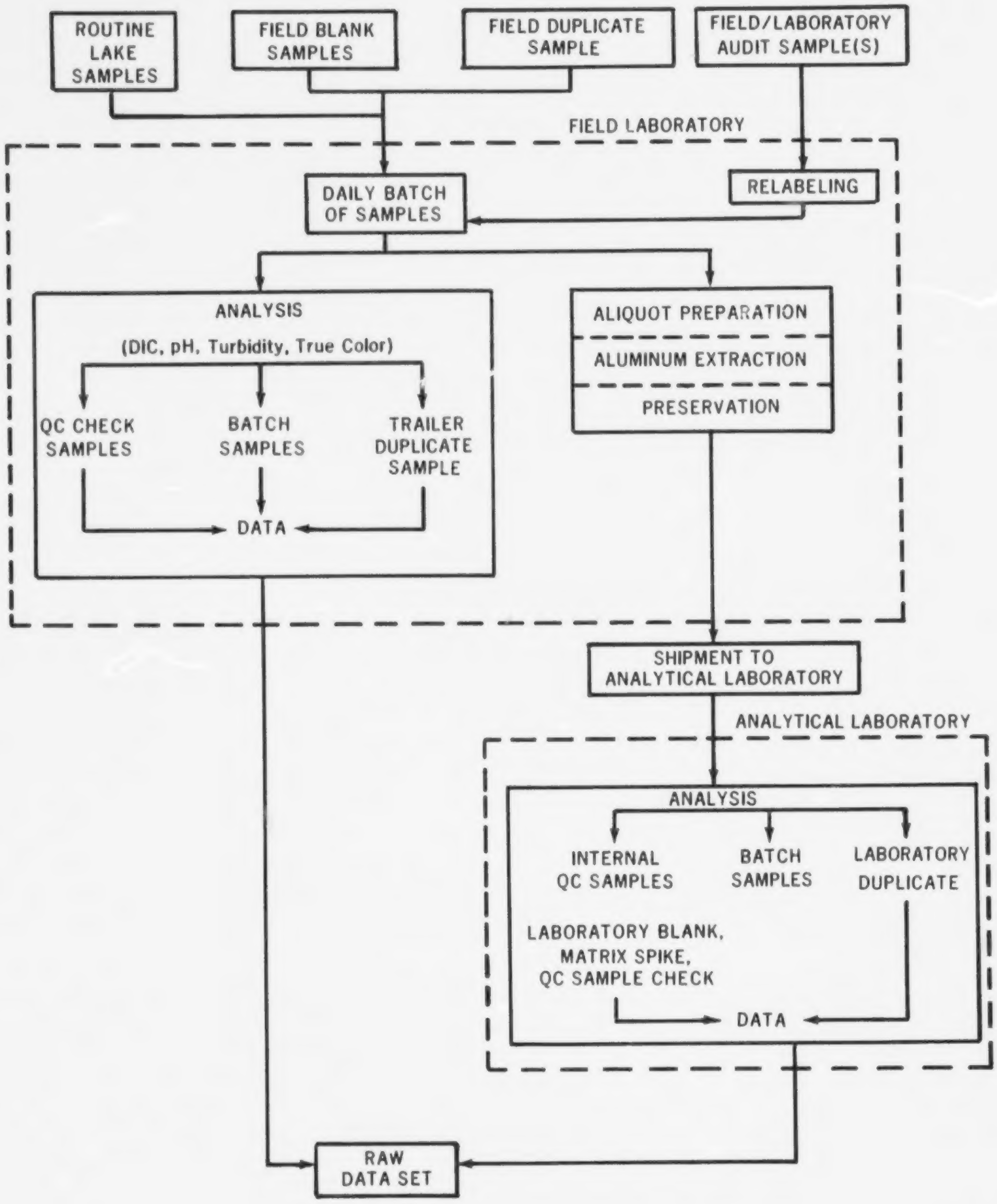

ROUTINE LAKE SAMPLES
FIELD BLANK SAMPLES
FIELD DUPLICATE SAMPLE
FIELD/LABORATORY AUDIT SAMPLE(S)
FIELD LABORATORY
DAILY BATCH OF SAMPLES
RELABELING
ANALYSIS
(DIC, pH, Turbidity, True Color)
QC CHECK SAMPLES
BATCH SAMPLES
TRAILER DUPLICATE SAMPLE
DATA
ALIQUOT PREPARATION
ALUMINUM EXTRACTION
PRESERVATION
SHIPMENT TO ANALYTICAL LABORATORY
ANALYTICAL LABORATORY
ANALYSIS
INTERNAL QC SAMPLES
BATCH SAMPLES
LABORATORY DUPLICATE
LABORATORY BLANK, MATRIX SPIKE, QC SAMPLE CHECK
DATA
RAW DATA SET

Figure 2. Flow of samples and data through field and analytical laboratories, Eastern Lake Survey - Phase I.

Filtration through a 0.45-μm membrane filter was used to remove suspended particulate and large colloidal material. This process provided subsamples that represented the dissolved fraction of analytes. Suspended material was filtered from these aliquots at the field laboratory because such material could have been a source of biological activity or, through dissolution, of additional analyte. It also could have provided surface area for adsorption or precipitation of dissolved analytes which would serve as a transport mechanism for removing these analytes from solution. Acid was added to some aliquots to prevent loss of dissolved analytes caused by precipitation or by chemical or biological reactions. Storage at 4°C was specified for aliquot 2 to reduce volatilization of the solvent and for aliquots 3 through 6 to reduce biological activity.

Field Laboratory Measurements

After the sample preparation and preservation steps were identified, it was necessary to establish maximum holding times to assure that the samples were analyzed before any significant degradation occurred.

Four parameters (pH, DIC, true color, and turbidity) were identified as requiring immediate analysis. Use of the mobile field laboratory for these analyses permitted all measurements to be completed within 16 hours of sample collection.

To assure that reliable measurements of DIC and pH were obtained, samples for those two field laboratory measurements were collected and were analyzed in a closed system within the shortest possible holding times. This procedure was followed to avoid problems with changes in dissolved inorganic carbon (DIC) content and thereby to represent accurately the in situ values.

True color and turbidity were determined in the field laboratory because the recommended holding time was 48 hours (U.S. EPA 1983). Turbidity had to be measured as soon as possible to avoid settling of suspended matter. True color and turbidity are subject to changes which are due to chemical activity and adsorption effects.

There is evidence that dissolved aluminum species change rapidly after sample collection (Driscoll et al. 1983); therefore, it was recommended that the aluminum extraction be performed in the field as soon as possible. It was not possible to perform the extraction in the helicopter because of concerns about exposure of the crew to MIBK vapors and the increased possibility of sample contamination. All samples were extracted in a laminar-flow hood in the field laboratory within 16 hours of collection.

ANALYTICAL LABORATORY QUALITY CONTROL PROTOCOLS

Analytical methods and quality control protocols were developed for use by the contract laboratories in accordance with the ELS-I research plan and the pilot study results. These methods and protocols are described below and are outlined in greater detail in the analytical methods manual and the QA plan.

In general, specific models of instruments were not required for the contract laboratories although the analytical methods manual contains particular recommendations for instruments in some methodologies. Instrumentation for all of the methods required some form of calibration. For all methods except conductance, a series of standards was analyzed and a calibration curve was calculated.

Several requirements for sample concentration ranges were specified for the analytical methods. The concentration range of the standards used to calculate the calibration curve was required to bracket the range of concentrations observed in the samples analyzed. If the concentration of analyte was at or below the detection limit, the concentration of the detection limit QC standard had to be between two and three times the detection limit. This QC requirement assured that the reported results were based upon interpolation within the calibration curve and not on extrapolation outside the curve which could result in significant error. The calibration required for conductance measurements was dependent upon the type of conductivity meter used and was either a single point calibration or was internally set by the factory.

Calibration of laboratory equipment was initially verified prior to sample analysis by analyzing an independent QC sample (either commercially or internally prepared). If the measured value for the QC sample was not within established control limits, new calibration standards were prepared, and, where applicable, a new calibration curve was generated. Calibration was also reverified on a routine basis by reanalyzing the QC sample after every 10 samples analyzed and after the last sample for the batch. If the measured value was not within established control limits, a new calibration was required, and all samples after the previous acceptable QC check had to be reanalyzed.

Sample Holding Times

A maximum sample holding time, determined from the time of sample collection to sample analysis, was established for each parameter measured in the analytical laboratories (Table 1). These holding times were based upon information from the literature, the best scientific judgment related to the defined needs, and the logistical demands and limitations of the ELS-I.

A 7-day holding time was specified for the contract analytical laboratory measurements of pH, nitrate, and total extractable aluminum. McQuaker et al. (1979) reported that the pH of a sample remains stable for up to 15 days if the sample is kept at 4°C and is sealed from the atmosphere; however, in the EPA manual Methods for Chemical Analysis of Water and Wastes (U.S. EPA 1983), it is recommended that the pH be measured immediately after sample collection. The same manual also specifies a 48-hour maximum holding time for nitrate in unpreserved (not acidified) water samples. Other sources (APHA 1985; Williams 1979; Quave 1980) indicate that nitrate is stable for 2 to 4 weeks if the sample is stored in the dark at 4°C. The 7-day holding time for pH and nitrate was selected as a limit that was practical with respect to the logistical constraints of the survey and that was conservative in relation to the available guidelines.

Barnes (1975) reported that the MIBK-aluminum extract is stable for several weeks following extraction. However, for the ELS-I, a 7-day holding time was specified for total extractable aluminum in order to minimize potential changes in sample composition which are due to volatilization of the MIBK.

A 14-day holding time was specified for measurements of ANC, BNC, conductance, DIC, and DOC; this holding time was based on U.S. EPA (1983) and on practical considerations with regard to the logistical design of the survey. The DIC measurements were performed almost simultaneously with the corresponding pH measurements in accordance with requirements in the analytical laboratory contract.

A 28-day maximum holding time was specified for the remaining contract analytical laboratory measurements. In many cases, especially for the metals, holding times up to 6 months are acceptable with proper sample handling and preservation (U.S. EPA 1983). However, the analytical laboratory contract required that the final data package be submitted within 35 days after receipt of the samples. A 28-day holding time was specified as a conservative limit to meet that contract requirement and to protect sample quality.

Reporting Requirements

As noted above, the contract analytical laboratories were required to analyze the samples and to report the results within 35 days after sample receipt. The reporting requirements included the submission of analytical results and specific information related to the maximum sample holding times discussed above. This information was used by the QA auditors to judge the performance of the laboratory and the quality of the data. The requirement for a specific delivery time ensured that the data packages were delivered in time to allow for preliminary review by the QA auditors and for corrective action, if necessary.

QUALITY ASSURANCE AND QUALITY CONTROL SAMPLES

The QA program utilized a variety of QA and QC samples. The numbers of QA and QC samples used in the survey were based on the need to keep program costs within reason while providing a maximum amount of information. The QC samples were used by field samplers and field laboratory personnel (Morris et al. 1986) and by analytical laboratory personnel (Drouse et al. 1986). QA sample data were used by the QA staff to evaluate the quality of routine sample analyses and to judge overall field and laboratory performance. Descriptions, functions, and frequencies of use of QA and QC samples are provided in Table 3.

FIELD LABORATORY AND ANALYTICAL LABORATORY ON-SITE EVALUATIONS

One or more on-site evaluations of each of the contract analytical laboratories and each of the field stations were performed by a QA audit team to assure that the sampling and analysis activities were being implemented as planned. These evaluations are described in Drousé et al. (1986).

TABLE 3. QUALITY ASSURANCE AND QUALITY CONTROL SAMPLES USED IN THE EASTERN LAKE SURVEY - PHASE I

Sample Type	Description	Function	Frequency of Use
Quality Assurance			
Field Blank	Reagent-grade deionized water[a] subjected to sample collection, processing and analysis	Used in estimating background due to sample collection, processing and analysis	One per sampling crew per day
Field Duplicate	Duplicate lake or stream sample	Used in estimating overall within-batch precision	One per field station per day
Field Audit	Synthetic sample or natural lake sample; processed at field lab	Used in estimating overall among-batch precision and lab bias	As scheduled
Laboratory Audit	Synthetic sample or natural lake sample; prepared at support lab	Used in estimating analytical among-batch precision and lab bias	As scheduled
Quality Control			
Calibration Blank	Reagent-grade deionized water[a]	Used in identifying signal drift and contamination of sample	One per lab batch
Reagent Blank	Reagent-grade deionized water[a] plus reagents for total Al, SiO_2 analyses	Used in identifying contamination of reagents	One per lab batch
Quality Control Check Sample (QCCS)	Standard solution from source other than calibration standard	Used in determining accuracy and consistency of instrument calibration	Before the first measurement and as specified
Detection Limit QCCS	Standard solution at 2 to 3 times the required detection limit	Used in determining accuracy at lower end of linear dynamic range of measurement method	One per lab batch
Field Laboratory (Trailer) Duplicate	Split of lake or stream sample	Used in determining analytical within-batch precision of field lab measurements	One per field batch
Analytical Laboratory Duplicate	Split of sample aliquot	Used in determining analytical within-batch precision of analytical lab measurements	One per lab batch
Matrix Spike	Sample aliquot plus known quantity of analyte	Used in determining sample matrix effect on analytical lab measurements	One per lab batch

[a] ASTM (1984b).

SECTION 3

DATA BASE QUALITY ASSURANCE

The data base for the ELS-I was managed by the Oak Ridge National Laboratory (ORNL) which has experience in managing large data bases, in manipulating data, and in restructuring data bases to satisfy data analysis needs. The data are stored in four major data sets: (1) a raw data set of field and analytical laboratory data, (2) a verified data set, (3) a validated data set, and (4) a final data set.

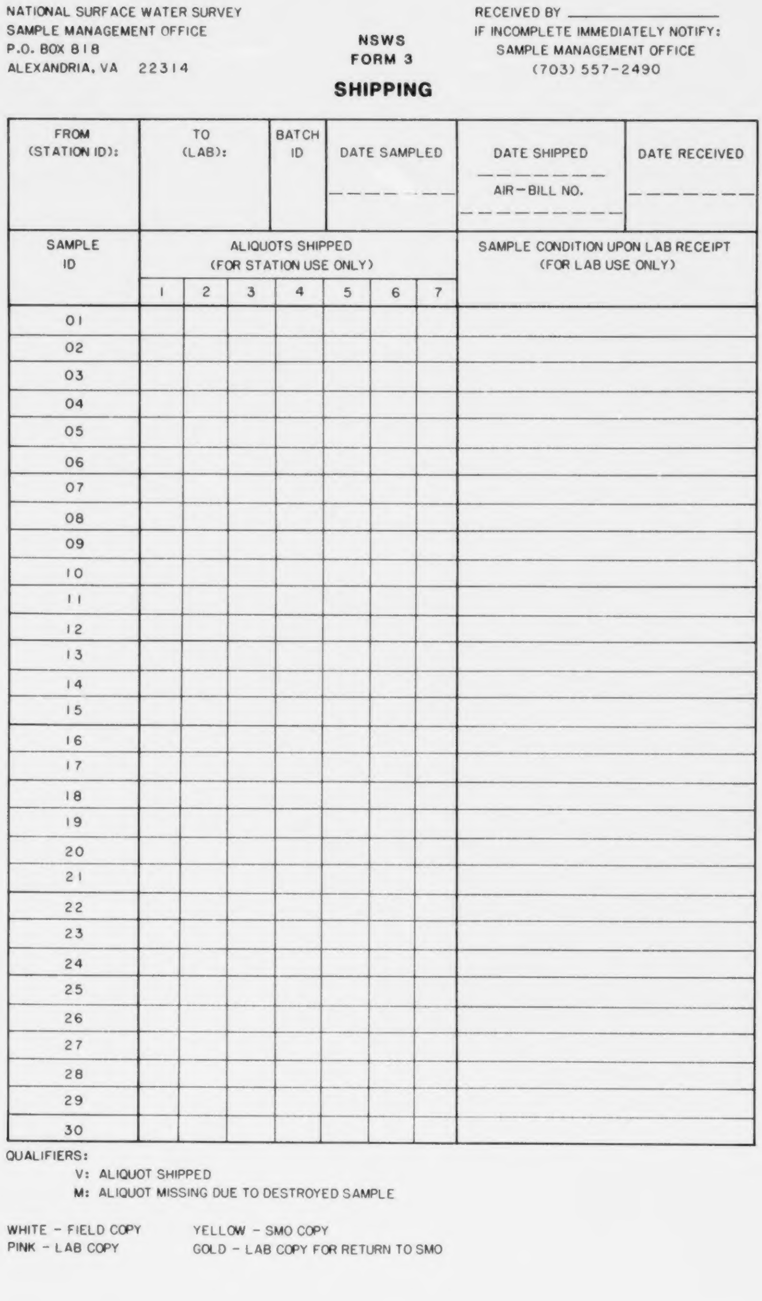
Development of the data base began when samples and data were transferred from the field stations to the analytical laboratories and it continued with receipt of the analytical results and the data verification reports. The process was complete after validation of the data by ERL-Corvallis. The final data set was generated from the validated data by using known relationships between physicochemical parameters (Linthurst et al. 1986). The final data set provided a representative summary of sample values for use in generating population estimates.

DATA AND SAMPLE TRANSFER

Data from in situ, field laboratory, and contract analytical laboratory measurements were transferred to ORNL and EMSL-LV initially in hardcopy form. Documentation related to shipment of samples from the field stations to the contract analytical laboratories was also transferred in this manner. After the appropriate information was entered into the data base, a magnetic tape containing raw data was sent to the EPA IBM 3081 computer at the National Computer Center (NCC), Research Triangle Park, North Carolina. Each tape received by the NCC tape library was assigned a volume serial number and a BIN number that indicated the physical location of the tape. The EMSL-LV QA staff then remotely loaded the tape to disk files and reviewed the data.

Transfer of Samples and Data From Field Stations

Following sample processing at the field laboratory, the aliquots were shipped in Styrofoam-lined shipping cartons with frozen freeze-gel packs to maintain a temperature of 4°C. A four-part carbonless shipping form (Figure 3) was completed for each shipping container. One copy was retained at the field station, one copy was sent to the U.S. EPA Sample Management Office (SMO), and two copies (sealed in a plastic bag) were enclosed in the carton. The shipping container was then sealed and shipped by overnight delivery to the contract analytical laboratory. Preserved splits of all samples were sent to ERL-Corvallis for chemical analysis by ICPES (J. L. Engels et al. in preparation). Additionally, splits of samples from selected regions were sent to two Canadian



NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3

SHIPPING

RECEIVED BY ________________
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

FROM (STATION ID):	TO (LAB):	BATCH ID	DATE SAMPLED	DATE SHIPPED	DATE RECEIVED
			_ _ _ _ _ _ _ _	_ _ _ _ _ _ _ _ AIR-BILL NO. _ _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _ _

SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)							SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	
01								
02								
03								
04								
05								
06								
07								
08								
09								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								

QUALIFIERS:
V: ALIQUOT SHIPPED
M: ALIQUOT MISSING DUE TO DESTROYED SAMPLE

WHITE - FIELD COPY
PINK - LAB COPY
YELLOW - SMO COPY
GOLD - LAB COPY FOR RETURN TO SMO

Figure 3. NSWS Form 3 - Shipping.

laboratories and to a Norwegian laboratory for chemical analysis (M. A. Stapanian et al. in preparation).

When the samples arrived at the designated contract laboratory, a receiving clerk recorded the date received on each shipping form, verified that the sample contents matched those listed on the shipping form, and completed the "sample condition" portion of the shipping form. The sample condition notation included such information as leakage, insufficient sample, noticeable suspended particulates, partially frozen samples, and internal temperature of each shipping container. The field laboratory coordinator was contacted immediately regarding any questionable conditions or discrepancies in the listed contents. Upon completion of sample inspection, the receiving clerk mailed one copy of each shipping form to SMO and retained the other copy.

In addition to shipping samples, the field laboratory personnel distributed data forms to various locations. Copies of the lake data form (Figure 4) and the field laboratory data form (Figure 5) were mailed to the QA manager and to ORNL. Upon receipt of the lake data and field laboratory data forms, ORNL personnel entered the data from these forms into the raw data set. This data flow scheme is summarized in Figure 6.

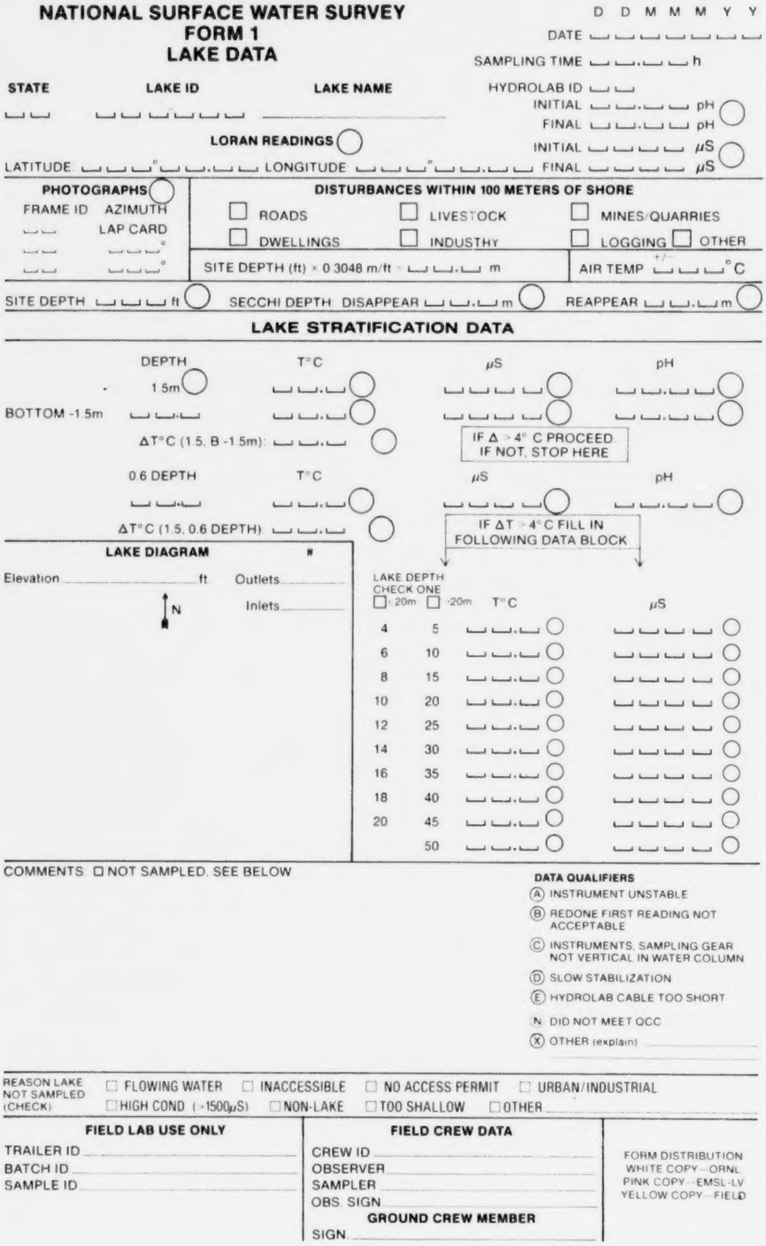
Transfer of Analytical Laboratory Data

After all analyses for a single batch of samples were completed, the analytical laboratory personnel prepared a report called a sample data package. All analytical results were recorded on the forms listed in Table 4. The laboratory manager was required to sign each form signifying that he or she had reviewed the data and that the samples were analyzed exactly as described in the contract. Any deviations from the contract required the authorization of the ELS-I QA manager prior to sample analysis. The data package also contained a narrative description of any difficulties encountered. All original raw data were retained by the laboratory manager until otherwise notified. Raw data included data system printouts, chromatograms, notebooks, QC charts, standard preparation data, and any other information pertinent to sample analysis. The original data package was retained by the laboratory, and copies were mailed to EMSL-LV, SMO, and ORNL.

Raw Data Set

At ORNL, the field and laboratory data and data qualifiers (Table 5) reported on Forms 1, 2, 11, 13, and 18 through 23 were directly entered into the data base by using Statistical Analysis System software (SAS Institute, Inc. 1985).

All data were entered independently by two different operators. A computer program (COMPARE) was developed to identify any inconsistencies between the two data sets (Rosen and Kanciruk 1985). The inconsistencies were then corrected using the SAS full-screen editing procedure. The purpose of this double entry and comparison process was to minimize data entry errors (Kanciruk et al. 1986b).



NATIONAL SURFACE WATER SURVEY
FORM 1
LAKE DATA

D D M M M Y Y
DATE
SAMPLING TIME h
HYDROLAB ID
INITIAL pH ○
FINAL pH
INITIAL μS ○
FINAL μS

STATE **LAKE ID** **LAKE NAME**

LORAN READINGS ○
LATITUDE ° . LONGITUDE ° .

PHOTOGRAPHS ○
FRAME ID AZIMUTH
LAP CARD

DISTURBANCES WITHIN 100 METERS OF SHORE
☐ ROADS ☐ LIVESTOCK ☐ MINES/QUARRIES
☐ DWELLINGS ☐ INDUSTRY ☐ LOGGING ☐ OTHER

SITE DEPTH (ft) × 0.3048 m/ft = . m
AIR TEMP +/− °C

SITE DEPTH ft ○ SECCHI DEPTH: DISAPPEAR . m ○ REAPPEAR . m ○

LAKE STRATIFICATION DATA

	DEPTH	T°C	μS	pH
	1.5m ○	. ○	○	. ○
BOTTOM -1.5m	.	. ○	○	. ○

ΔT°C (1.5, B -1.5m): . ○

IF Δ > 4° C PROCEED
IF NOT, STOP HERE

0.6 DEPTH	T°C	μS	pH
.	. ○	○	. ○

ΔT°C (1.5, 0.6 DEPTH): . ○

IF ΔT > 4°C FILL IN
FOLLOWING DATA BLOCK

LAKE DIAGRAM #
Elevation ft Outlets
Inlets
N

LAKE DEPTH
CHECK ONE

☐ <20m	☐ >20m	T°C	μS
4	5	. ○	○
6	10	. ○	○
8	15	. ○	○
10	20	. ○	○
12	25	. ○	○
14	30	. ○	○
16	35	. ○	○
18	40	. ○	○
20	45	. ○	○
	50	. ○	○

COMMENTS: ☐ NOT SAMPLED, SEE BELOW

DATA QUALIFIERS
- Ⓐ INSTRUMENT UNSTABLE
- Ⓑ REDONE FIRST READING NOT ACCEPTABLE
- Ⓒ INSTRUMENTS, SAMPLING GEAR NOT VERTICAL IN WATER COLUMN
- Ⓓ SLOW STABILIZATION
- Ⓔ HYDROLAB CABLE TOO SHORT
- Ⓝ DID NOT MEET QCC
- Ⓧ OTHER (explain)

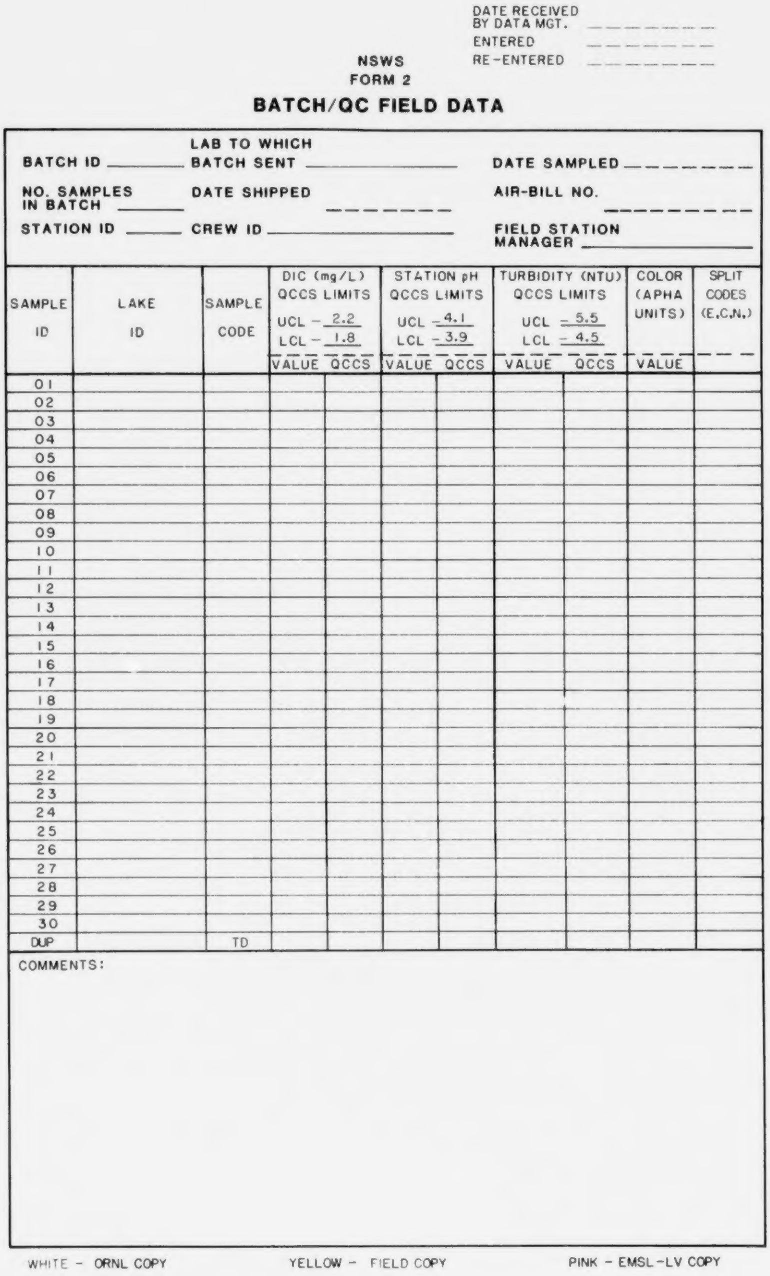
REASON LAKE NOT SAMPLED (CHECK)
☐ FLOWING WATER ☐ INACCESSIBLE ☐ NO ACCESS PERMIT ☐ URBAN/INDUSTRIAL
☐ HIGH COND (>1500μS) ☐ NON-LAKE ☐ TOO SHALLOW ☐ OTHER

FIELD LAB USE ONLY
TRAILER ID
BATCH ID
SAMPLE ID

FIELD CREW DATA
CREW ID
OBSERVER
SAMPLER
OBS. SIGN
GROUND CREW MEMBER
SIGN.

FORM DISTRIBUTION
WHITE COPY—ORNL
PINK COPY—EMSL-LV
YELLOW COPY—FIELD

Figure 4. NSWS Form 1 - Lake Data.



DATE RECEIVED BY DATA MGT. ________
ENTERED ________
RE-ENTERED ________

NSWS
FORM 2

BATCH/QC FIELD DATA

BATCH ID ________
LAB TO WHICH BATCH SENT ________
DATE SAMPLED ________
NO. SAMPLES IN BATCH ________
DATE SHIPPED ________
AIR-BILL NO. ________
STATION ID ________
CREW ID ________
FIELD STATION MANAGER ________

SAMPLE ID	LAKE ID	SAMPLE CODE	DIC (mg/L) QCCS LIMITS UCL – 2.2 LCL – 1.8		STATION pH QCCS LIMITS UCL – 4.1 LCL – 3.9		TURBIDITY (NTU) QCCS LIMITS UCL – 5.5 LCL – 4.5		COLOR (APHA UNITS)	SPLIT CODES (E,C,N.)
			VALUE	QCCS	VALUE	QCCS	VALUE	QCCS	VALUE	
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
DUP		TD								

COMMENTS:

WHITE – ORNL COPY
YELLOW – FIELD COPY
PINK – EMSL-LV COPY

Figure 5. NSWS Form 2 - Field Laboratory Data.

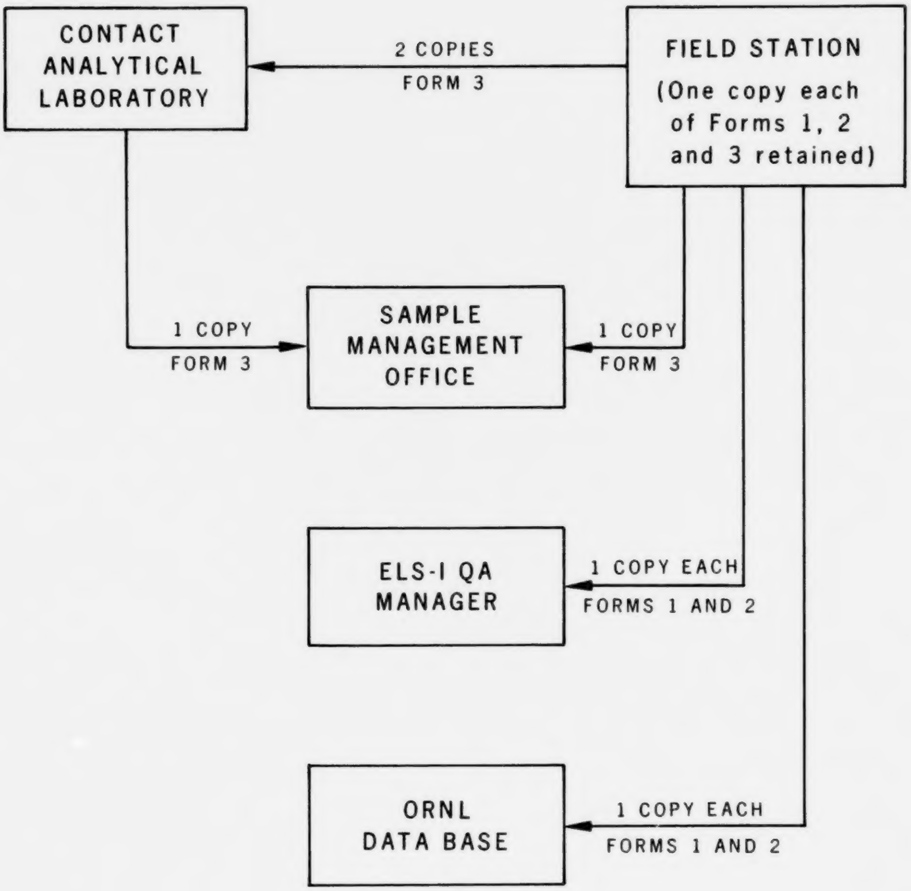

CONTACT ANALYTICAL LABORATORY
2 COPIES
FORM 3
FIELD STATION
(One copy each of Forms 1, 2 and 3 retained)
1 COPY
FORM 3
SAMPLE MANAGEMENT OFFICE
1 COPY
FORM 3
ELS-I QA MANAGER
1 COPY EACH
FORMS 1 AND 2
ORNL DATA BASE
1 COPY EACH
FORMS 1 AND 2

Figure 6. Eastern Lake Survey - Phase I data flow scheme.

TABLE 4. LIST OF DATA FORMS USED BY ANALYTICAL LABORATORIES IN THE EASTERN LAKE SURVEY - PHASE I[a]

Data Form	Description
11	Summary of Sample Results
13	ANC and BNC Results
14[b]	QC Data for ANC and BNC Analyses
15[b]	Conductance (Measured and Calculated)
16[b]	Anion-Cation Balance Calculations
17	Ion Chromatography Resolution Test
18	Instrumental Detection Limits
19	Sample Holding Time Summary
20	Results of Blank Sample and QCCS Analyses
21	Results of Matrix Spike Analyses
22	Results of Duplicate Sample Analyses
23	Results of Standard Additions Analyses

[a] These forms are shown in Drousé et al. (1986).

[b] Form not required to be submitted with data package but recommended for internal QC requirements.

TABLE 5. FIELD AND LABORATORY DATA QUALIFIERS ('TAGS') USED IN THE EASTERN LAKE SURVEY - PHASE I

Qualifier	Indicates
A	Instrument unstable
B	Redone, first reading not acceptable
C	Instruments, sampling gear not vertical in water column
D	Slow stabilization
E	Hydrolab cable too short
F	Result outside QA criteria (with consent of QA manager)
G	Result obtained from method of standard additions
H	Holding time exceeded criteria (Form 19 only)
J	Result not available; insufficient sample volume shipped to laboratory from the field
K	Result not available; entire aliquot not shipped
L	Not analyzed due to interference
M	Result not available; sample lost or destroyed by lab
N	Not required
P	Result outside QA criteria, but insufficient volume for reanalysis
Q	Result outside QA criteria
R	Result from reanalysis
S	Contamination suspected
T	Leaking container
U	Result not required by procedure; unnecessary
V	Anion-cation balance outside criteria due to high DOC
W	Percent Difference (%D) calculation (Form 14) outside criteria due to high DOC
X	Available for miscellaneous comments in the field only
Y	Available for miscellaneous comments in the field only
Z	Available for miscellaneous comments in the field only
<	Measurements taken at <1.5 m

DATA VERIFICATION

Verification procedures for the raw data set were developed and implemented by the EMSL-LV QA staff. The objective of data verification was to identify and correct, qualify, or eliminate data of unacceptable quality. Data qualifiers added during the verification process ('flags') are listed in Table 6. This objective was accomplished by using the following organized process to examine the data: (1) establish daily communication with the field and analytical laboratories, (2) verify completeness and consistency of the data package on receipt, and review any comments or questions associated with the batch or sample under evaluation (i.e., tags and narrative comments), (3) evaluate preliminary QA sample data and routine sample data, (4) obtain confirmation, correction, or reanalysis data from the laboratories as needed to address atypical values, and (5) provide correcting entries to ORNL for establishing the verified data set. A computer software package (AQUARIUS) was developed to automate this procedure as much as possible (Fountain and Hoff 1985). The AQUARIUS package was tested during the ELS-I and is being modified to provide additional verification procedures for other phases of the NSWS.

Data verification procedures are summarized below and are illustrated in Figure 7. Additional details are provided in Drousé et al. (1986).

Daily Communication

Daily communication was maintained between the EMSL-LV QA staff and each contract analytical laboratory during the periods when samples were being analyzed. The objectives of daily communication were to assure that the laboratory was implementing the QC requirements and to obtain a preliminary evaluation of data quality and laboratory performance. Performance was judged by reviewing the analytical results for QA samples (e.g., field blanks, field duplicates, and audit samples). Daily contact enabled the QA auditors to be familiar with analytical problems and preliminary data in order to initiate data analysis prior to receipt of the data package. The bulk of the data evaluation occurred concurrently with the input of the raw data by ORNL.

Data Receipt

As noted above, the QA staff at EMSL-LV received copies of the field data forms (Forms 1 and 2) from each field laboratory coordinator. Upon receipt, the auditor checked for the following items:

- Lake ID. The lake data form (Form 1) was compared with the field laboratory data form (Form 2) for transcription errors.
- Trailer Duplicate. The duplicate lake sample ID recorded on Form 2 had to match a routine lake sample ID, and the precision criteria for pH, DIC, true color, and turbidity between those two samples had to be achieved.
- Hydrolab Calibration Data. The Hydrolab pH and conductance QCCS values from Form 1 were compared with the data from the Hydrolab calibration forms to assure that initial calibration criteria were met or that data qualifiers were added.

TABLE 6. VERIFICATION DATA QUALIFIERS ('FLAGS') USED IN THE EASTERN LAKE SURVEY - PHASE I

A0	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to unknown cause.
A1	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to nitrate contamination.
A2	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to anion (other than nitrate) contamination.
A3	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to cation contamination.
A4	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to unmeasured organic protolytes (fits Oliver Model).
A5	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too high (list suspect anion).
A6	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too low (list suspect cation).
A7	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too low (list suspect anion).
A8	Anion-Cation Percent Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too high (list suspect cation).
B0	External (field) blank is above expected criteria for pH, DIC, DOC, conductance, ANC, and BNC determinations.
B1	Internal (lab) blank is >2 x RDL for pH, DIC, DOC, conductance, ANC, and BNC determinations.
B2	External (field) blank is above expected criteria and contributed >20% to sample values. (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations.)
B3	Internal (lab) blank is >2 x RDL and contributes >10% to the sample concentrations. (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations.)
B4	Potential negative sample bias based on internal (lab) blank data.

(continued)

TABLE 6. (continued)

B5	Potential negative sample bias based on external (field) blank data.
C0	Percent Conductance Difference (%CD) is outside criteria due to unknown cause (possible analytical error - ion concentration too high).
C1	Percent Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too high (list suspect anion).
C2	Percent Conductance Difference (%CD) is outside criteria due to anion contamination.
C3	Percent Conductance Difference (%CD) is outside criteria due to cation contamination.
C4	Percent Conductance Difference (%CD) is outside criteria due to unmeasured organic anions (fits Oliver Model).
C5	Percent Conductance Difference (%CD) is outside criteria due to possible analytical error in conductance measurement.
C6	Percent Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too low (list suspect anion).
C7	Percent Conductance Difference (%CD) is outside criteria due to unmeasured protolyte anions (does not fit Oliver Model).
C8	Percent Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too low (list suspect cation).
C9	Percent Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too high (list suspect cation).
D0	External (field) duplicate precision exceeded the maximum expected percent relative standard deviation (%RSD), but either the routine or the duplicate concentrations were <10 x RDL.
D2	External (field) duplicate precision exceeded the maximum expected percent relative standard deviation (%RSD), and both the routine and duplicate sample concentrations were ≥10 x RDL.
D3	Internal (lab) duplicate precision exceeded the maximum allowable percent relative standard deviation (%RSD), and both the routine and duplicate sample concentrations were ≥10 x RDL.

(continued)

TABLE 6. (continued)

F0	Percent Conductance Difference (%CD) exceeded criteria when Hydrolab conductance value was substituted.
F1	Hillman-Kramer protolyte analysis program indicated field pH problem when Hydrolab pH value was substituted.
F2	Hillman-Kramer protolyte analysis program indicated unexplained field pH or DIC problem when Hydrolab pH value was substituted.
H0	The maximum holding time criteria were not met.
H1	No "Date Analyzed" data were submitted for reanalysis data.
L1	Instrumental Detection Limit (IDL) exceeded RDL and sample concentration was <10 x IDL.
M0	Value was obtained using a method which is unacceptable by the contract.
N0	Audit sample value exceeded upper control limit.
N1	Audit sample value was below control limit.
N2	Audit sample value exceeded control limits due to suspect audit sample preparation.
N5	NO_3^- data obtained from analysis of aliquot 5.
P0	Field problem - station pH.
P1	Field problem - station DIC.
P2	Field problem - unexplained pH or DIC.
P3	Lab problem - initial ANC pH.
P4	Lab problem - initial BNC pH.
P5	Lab problem - unexplained - initial pH (ANC or BNC).
P6	Lab problem - initial DIC.
P7	Lab problem - air-equilibrated pH or DIC.

(continued)

TABLE 6. (continued)

P8	Lab problem - unexplained - initial pH or DIC.
P9	Lab problem - ANC determination.
Q1	Quality control check sample (QCCS) was above contractual criteria.
Q2	Quality control check sample (QCCS) was below contractual criteria.
Q3	Number of quality control check samples (QCCS) measured was insufficient.
Q4	No quality control check sample (QCCS) analysis was performed.
S0	Matrix spike percent recovery (%REC) was above contractual criteria.
S1	Matrix spike percent recovery (%REC) was below contractual criteria.
V	Data verified.

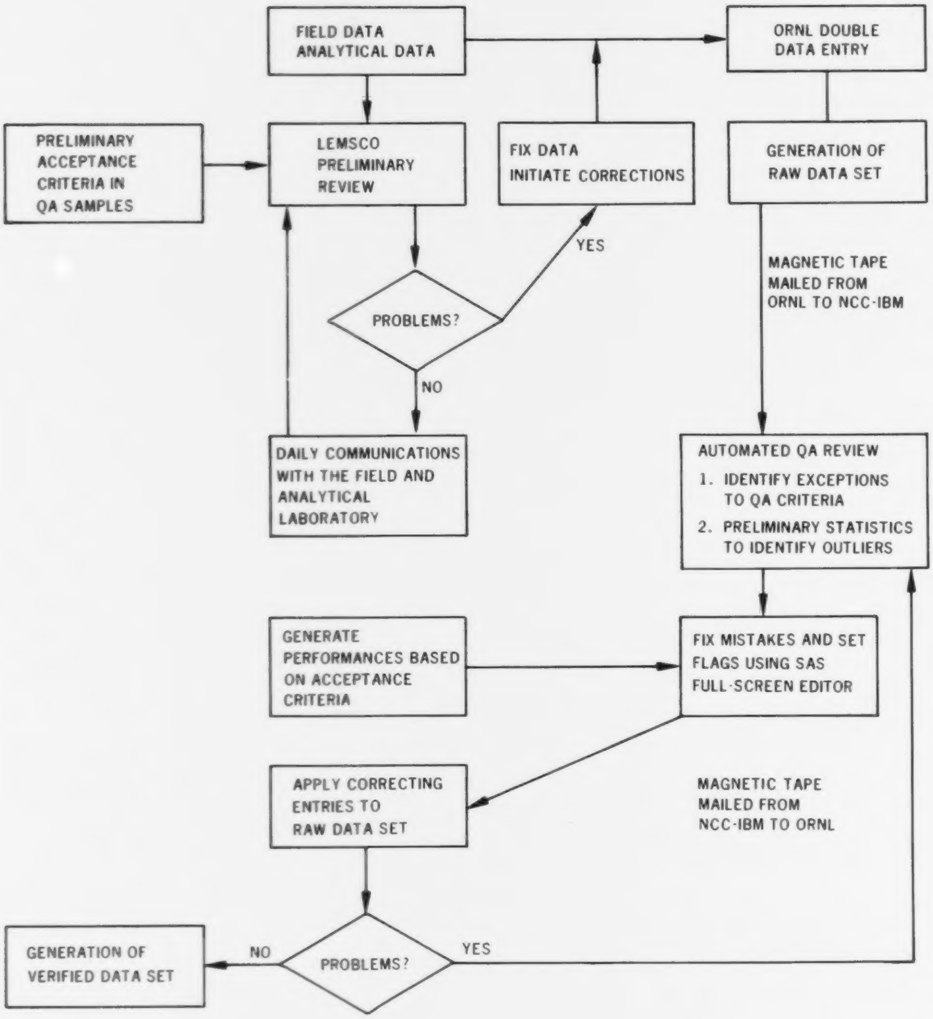

FIELD DATA
ANALYTICAL DATA
ORNL DOUBLE DATA ENTRY
PRELIMINARY ACCEPTANCE CRITERIA IN QA SAMPLES
LEMSCO PRELIMINARY REVIEW
FIX DATA INITIATE CORRECTIONS
GENERATION OF RAW DATA SET
YES
MAGNETIC TAPE MAILED FROM ORNL TO NCC-IBM
PROBLEMS?
NO
DAILY COMMUNICATIONS WITH THE FIELD AND ANALYTICAL LABORATORY
AUTOMATED QA REVIEW
1. IDENTIFY EXCEPTIONS TO QA CRITERIA
2. PRELIMINARY STATISTICS TO IDENTIFY OUTLIERS
GENERATE PERFORMANCES BASED ON ACCEPTANCE CRITERIA
FIX MISTAKES AND SET FLAGS USING SAS FULL-SCREEN EDITOR
APPLY CORRECTING ENTRIES TO RAW DATA SET
MAGNETIC TAPE MAILED FROM NCC-IBM TO ORNL
GENERATION OF VERIFIED DATA SET
NO
PROBLEMS?
YES

Figure 7. Data verification process for the Eastern Lake Survey - Phase I.

- Hydrolab pH. The Form 1 pH value at 1.5 meters was compared with the field laboratory (Form 2) pH values. Values were expected to agree within 0.5 pH unit.

- Field laboratory pH and DIC. Form 2 values for field audit samples were compared with acceptance criteria. Routine/field duplicate pairs and routine/trailer duplicate pairs were evaluated for precision.

- pH and DIC QCCS Data. Form 2 QCCS data were compared with acceptance criteria.

Data anomalies were reported to the field laboratory coordinator for review. Continual review by the field laboratory staff minimized the number of data transcription errors encountered by the EMSL-LV QA staff. Data reporting errors were reported to ORNL for correction before values were entered into the data base. All telephone communications were documented in a bound notebook. Data changes were annotated on the appropriate form.

The contract laboratory data packages were delivered to the EMSL-LV QA staff upon completion of analysis or within 35 days following sample receipt. As they were received, data packages were reviewed for completeness, internal QC compliance, and appropriate use of data qualifiers. A data package completeness checklist was used by each EMSL-LV QA auditor to assure consistency in the review of all data packages (Figure 8). Problems were reported to the appropriate contract laboratory manager for corrective action. Comments provided by the laboratory with the data package were also reviewed to determine their impact on data quality and the need for any follow-up action by the laboratory. Completion of this checklist was important in verifying that the laboratory had met all contractual requirements for the purpose of payment.

Quality Assurance and Quality Control Data

ORNL personnel entered the data into the raw data set as the data packages were received. During the data entry period, QA sample data were evaluated by the EMSL-LV QA staff to establish performance-based acceptance criteria. The review process utilized the computer programs listed in Table 7 to identify or flag results that were exceptions to the expected QA-QC limits. These programs automated much of the QA review process and enabled the auditor to concentrate more effort on the correction or flagging of questionable data.

The QA auditor used the output from these programs (along with the original data and field notebooks) to evaluate the data and to complete the NSWS verification report contained in the QA plan. The verification report was actually a worksheet designed to systematically guide the auditor through the verification process. It listed procedures for qualifying ('flagging') data and for tracking both requests for confirmation reanalysis and for data resubmissions. It also listed the steps used to help explain the QA exceptions and to summarize all modifications to the raw data set. These auditing procedures are described in detail in Drousé et al. (1986).

NATIONAL SURFACE WATER SURVEY

Page 1 of 2

Data Package Completeness Checklist

Lab Name: ______________________ Batch ID: ______________________

Date: ______________________ Auditor's Initials: ______________________

	Yes	Partial	No	Comments
1. All major difficulties during analyses have been discussed with the QA manager or designee.				
2. Anion-cation balance and conductance balance checks exceeding criteria are reported on cover letter.				
3. a. Required forms (11, 13, 17, 18-23) submitted.				
b. Lab name, batch ID, and lab manager's signature submitted on all forms.				
c. Sample ID reported on Forms 13, 21, 22, and 23.				
d. Analyst's signature on Form 13.				
e. Correct units indicated on all forms.				
4. Form 11: a. Correct number of samples analyzed and results for each parameter tabulated.				
b. Data qualifiers (J, K, M, or U) reported when results are missing.				
c. Data qualifier R is reported when a sample is reanalyzed for QC purposes.				
d. F is reported as a data qualifier when a result is outside criteria (with consent of QA manager).				
e. G is reported as a data qualifier when the method of standard additions is used and Form 23 is submitted.				
f. ANC initial pH and BNC initial pH are within ±0.1 pH unit.				
5. Percent IC resolution reported as greater than 60% on Form 17.				
6. Form 18: a. Instrumental detection limits and associated dates of determination tabulated.				
b. Instrumental detection limits less than or equal to the required detection limits (Table 1-1).				
7. Form 19: a. Date sampled, date received, holding time plus date sampled, and dates of analyses for the correct number of samples are tabulated.				

(continued)

Figure 8. NSWS Data Package Completeness Checklist.

Page 2 of 2

	Yes	Partial	No	Comments
b. Date analyzed is less than or equal to the reported holding time plus date sampled.				
c. The data qualifier H is reported for dates of analyses which exceed the holding time plus date sampled with consent of QA manager.				
8. Form 20: a. Calibration blanks, reagent blanks, and DL QCCS are reported where required.				
b. Calibration blanks and reagent blanks are less than 2 times the required DL.				
c. DL QCCS is approximately 2 times the required DL and the measured values are within 20% of the theoretical values.				
d. QCCS true values are in the midrange of sample values.				
e. If high QCCS true values are reported, the samples analyzed on high range are discussed in the cover letter.				
f. Diluted samples and their dilution factors are discussed in the cover letter.				
9. Percent recovery of matrix spikes is reported on Form 21 for each required analysis, and the values are within the range of 85% to 115%.				
10. Duplicate precision results are reported for each parameter and are less than or equal to the maximum %RSD (Table 1-1).				
11. Standard additions are performed and Form 23 is submitted when the matrix spike analyses do not meet contract requirements.				

Note: Checklist is not required in data package but is recommended to be included in the raw data.

Figure 8. (continued).

TABLE 7. EXCEPTION IDENTIFICATION AND DATA REVIEW PROGRAMS USED IN THE EASTERN LAKE SURVEY - PHASE I

Title	Sample Type
Audit Sample Summary	(LH,LL,FH,FL,FN)
Lab and Field Blank Summary	(B,LB,FB)
Field Duplicate Precision Summary	(R,D Pairs)
Instrumental Detection Limit Summary	(All)
Holding Time Summary	(All)
DIC Check Calculations	(All)
ANC Check Calculations	(All)
Conductivity Check Calculations	(All)
Anion-Cation Balance Calculations	(All)
Batch QA-QC Summary	(All)
Comparison of Form 1 and Form 2	(pH and DIC)
Comparison of Form 2 and Form 11	(pH and DIC)
Protolyte Analysis - (DIC, DOC, pH, ANC, and BNC Data Evaluation)	
Audit Sample Window Generation	
Raw Data Listing - Format for QA Manager	
Complete Raw Data Listing - Format for Audit Staff	
Reagent-Calibration Blanks and QCCS	
Calculation of Laboratory Penalties	
Matrix Spike Summary	

After being entered into the raw data set, the data were reviewed on a batch basis by making use of both computer programs and manual review. These efforts checked internal consistency (e.g., ion balance difference and conductance difference) for each sample and the acceptability of both the QA sample data and the laboratory QC data for each batch. Examination of univariate distributions was also performed on QA sample data to identify statistical outliers and to establish or update performance acceptance criteria. Samples which met acceptance criteria for these checks were transferred into the verified data set.

When exceptions could be explained by the presence of organic compounds based on the Oliver model (Oliver et al. 1983) or on a correctable reporting error, the values associated with these samples were qualified or corrected and entered into the verified data set. This was accomplished through the Hillman-Kramer Protolyte Analysis Program as described in Drousé et al. (1986). When exceptions to the ion balance difference or conductance difference criteria could not be explained by calculated organic ion concentrations, that sample was reanalyzed to determine if the result was due to reporting or analytical error.

Suspected analytical errors were referred to the analytical laboratory for reanalysis. Acceptable values from reanalysis were qualified and substituted for the original values in the verified data set. For each parameter, samples that were not analyzed within maximum allowable holding times or that were associated with unacceptable QC or QA sample results were flagged before entry into the verified data set.

When the QA sample for a given parameter did not meet the acceptance criteria, that parameter was flagged for all samples in the batch. A parameter was also flagged when internal QC checks were not met. Those checks included matrix spike recovery, calibration and reagent blank analysis, internal duplicate precision, required instrumental detection limit, QCCS percent recovery, and maximum allowable holding times. In all cases, each flag generated by the computer was reviewed by the QA auditor for reasonableness and consistency before it was added to the data base.

Follow-up with Contract Analytical Laboratories

Completion of Step 2 (data receipt) and Step 3 (QA-QC review of data) included communications with the appropriate contract analytical laboratory. This follow-up (Step 4) was needed to obtain corrections to the data package, confirmation or correction of reported data, and sample reanalysis when required. Step 4 was the most difficult and time-consuming process in data verification, especially if the requests to the laboratory were not clearly supported by contract requirements. Typically, responses to requests for confirmation or correction of reported data were completed within 2 to 4 weeks. Reanalyses were either completed within 2 to 3 months or were not performed. Although every effort was made to identify samples for reanalysis within the maximum allowable holding times, the contract laboratory often had to choose between samples in progress and samples for reanalysis. Therefore, many reanalyses, especially for nitrate in aliquot 5, were performed outside the maximum allowable holding time.

Preparation and Delivery of Verification Tapes

After the first four verification steps were completed by the EMSL-LV QA staff, the data were adequate for establishing the verified data set. In order to translate the raw data set into the verified data set, a method for quickly transferring the information from EMSL-LV to ORNL was required. Changes to the raw data set were made by using computer entries called tuples. A tuple is an ordered group of elements (e.g., batch ID, sample ID, variable, old flag, new flag, old value, new value). For the ELS-I, tuples identified changes to a data set such as adding, changing, or deleting sample values or data qualifiers. A tuple was also created when a computer program generated a flag for a specific parameter.

The system that was used for modifying the ORNL raw data set was designed to minimize data entry errors. This system used separate areas for each program-generated tuple and each manual tuple (value change or deletion), which facilitated searching, modifying, and checking of tuple listings. When a tuple listing was ready to be sent to ORNL, a computer program (Database Administrator Program) was used to combine all of the tuple areas including flags, tags (data qualifiers added to a value in the field), and value changes, and to append the listing to the data base. This listing included only those tuples for which the batch ID, sample ID, variable name, and old value from EMSL-LV matched those from ORNL. The combined tuple was then written on magnetic tape and was mailed to ORNL from the NCC, RTP, North Carolina. ORNL processed the combined tuple listing and returned a magnetic tape to RTP with a listing of unmatched tuples which were mistakes that could not be applied to the data base until they were corrected. This cycle took about 10 days.

The overall outcome of the five steps described above was a verified data set in which all values which did not meet criteria were flagged, replaced with either corrected or reanalyzed data, or replaced with missing value codes (Table 8). Confirmation (C) and reanalysis (R) codes were removed from the data set when the correct values were received from the contract laboratory.

DATA VALIDATION

The data validation process identified potential errors in chemical analyses that could not be revealed by the verification procedures. These values included potential outliers and systematic errors because data were evaluated on a regional basis (Table 9). The quality of non-chemical variables was also evaluated during the validation process (Table 10).

Data validation was a joint activity performed by ERL-Corvallis and EMSL-LV. While interpreting the results, the data users identified questionable data points (Figure 9). The atypical data points were reported to the EMSL-LV QA staff who then reviewed the data packages and QA information to reverify the quality of that particular value. The final decisions regarding data quality were made by the EPA data users at ERL-Corvallis on the basis of all available information.

TABLE 8. MISSING VALUE CODES USED IN THE EASTERN LAKE SURVEY - PHASE I

A - Carbonate alkalinity, CO_2-acidity, and mineral acidity data are eliminated from data base because of method inconsistencies.

C - Temporary flag indicating raw data incomplete pending CONFIRMATION by analytical laboratory.

N - Eliminate from data base pending review of aliquot 5 nitrate data.

R - Temporary flag indicating raw data incomplete pending REANALYSIS.

X - Permanent flag indicating INVALID data based on QA review.

. - Value never reported.

(NOTE: These codes appear in NUMERIC fields only.)

The data validation process included the identification of possible outliers and the evaluation of possible systematic error in the measurement process. Both of these aspects were exploratory (as opposed to test-oriented). Thus, the validation methods stressed visual presentation and subjective, although conservative, data selection procedures. The objective was to identify data values or sets of data values that warranted special attention or caution when used for analysis of survey results or when used for model-building based upon survey data. The methods selected for detection of outliers and systematic errors were chosen for simplicity of computation by using pre-existing software whenever possible (see Figure 9). Data validation is discussed in greater detail in Drousé et al. (1986) and in Eilers et al. (1986).

DATA BASE REVIEW

Routine and duplicate data from each of the four data sets (raw, verified, validated, and final) that constitute the ELS-I data base were inspected by an independent data audit team. The data base review included an evaluation of how adequate the documentation was for value changes that were made between the raw and the final data sets. For some of the parameters, the documentation was evaluated by a search and review of all of the data. For other parameters, the documentation was evaluated by selecting a random subsample of the changed values for review. The review was a comparison of the old and the new values against the field and laboratory records and the verification reports.

The review also included a determination of the correctness of data entry. This was accomplished on a random sample of 25 lakes by reentering the Form 2 (Batch/QC Field Data) values for 12 parameters and checking those values against the values in the raw data set. The completeness of the data base was estimated for each of the parameters by examining the justifications for missing value codes. The correctness of the calculations of population estimates was verified by implementing the estimation algorithms on a test data set which was a subset of the final ELS-I data set.

TABLE 9. DATA VALIDATION FOR THE EASTERN LAKE SURVEY - PHASE I: COMPARISON OF VARIABLES USED TO CHECK FOR RANDOM AND SYSTEMATIC ERRORS

Conductance (analytical laboratory)	vs.	Conductance (field) Calculated conductance Sum of cations Sum of anions Ca Ca plus Na pH (field laboratory) ANC DIC
ANC	vs.	Ca pH (all measures) Sum of cations Sum of anions Calculated ANC [sum of base cations minus (SO_4^{2-} and Cl^-)]
pH (field laboratory)	vs.	pH (all measures) Sum of cations Sum of anions Al (extractable) SO_4^{2-} (expressed as percent of total anions)
DOC	vs.	True color Anion deficit Secchi disk transparency Turbidity
True color	vs.	Anion deficit Secchi disk transparency Turbidity
Turbidity	vs.	Secchi disk transparency
Ca	vs.	Mg SiO_2
Na	vs.	Cl^-
DIC (air-equilibrated)	vs.	DIC (initial)
Al (total)	vs.	Al (total extractable)

TABLE 10. PHYSICAL PARAMETERS USED IN THE VALIDATION PROCESS FOR THE EASTERN LAKE SURVEY - PHASE I

Parameter	General Description of Validation Checks
Latitude, Longitude	Lake location as measured by LORAN was compared against location on U.S.G.S. maps.
Lake Elevation, Lake Area, Watershed Area, Site Depth, Stream Inlets and Outlets, Lake Hydrologic Type	Lake and watershed characteristics were checked against state records, where available, to confirm lake identification.
Shoreline Land Use	Compared against aerial photographs
Water Temperature	Compared against range of appropriate temperature
Secchi Disk Transparency, True Color, Turbidity	Compared with each other for internal consistency

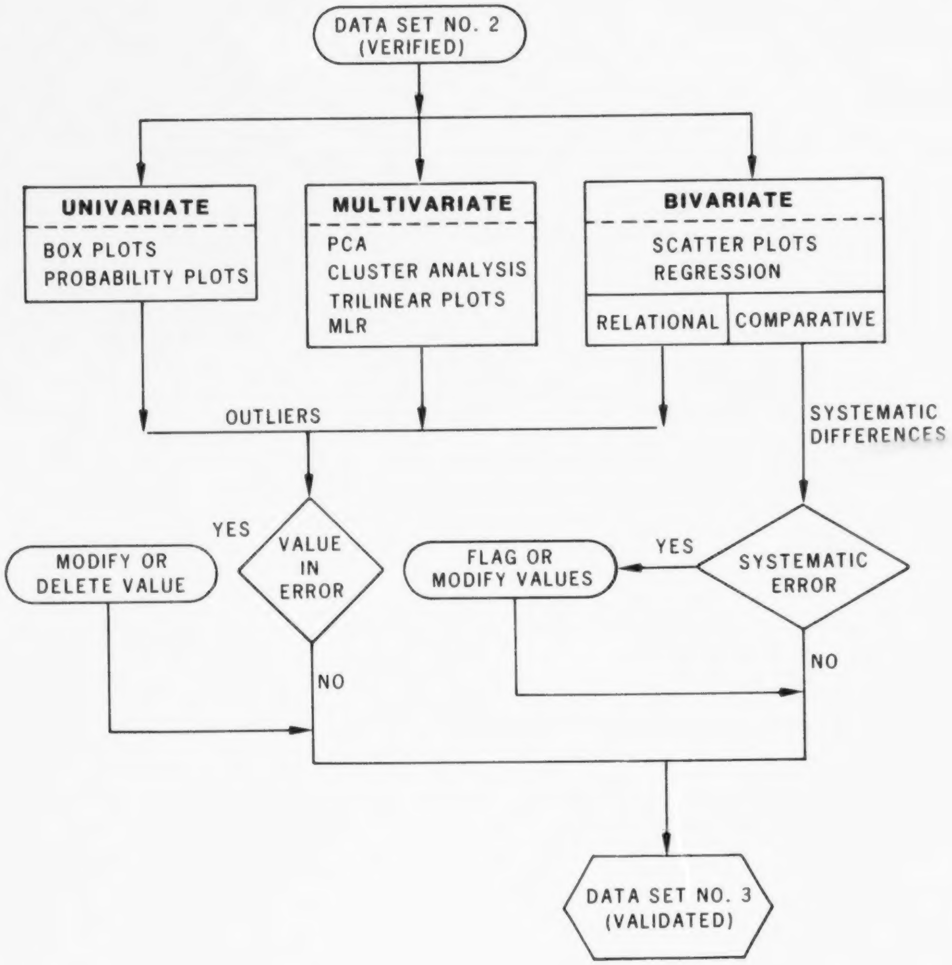

DATA SET NO. 2
(VERIFIED)
UNIVARIATE
BOX PLOTS
PROBABILITY PLOTS
MULTIVARIATE
PCA
CLUSTER ANALYSIS
TRILINEAR PLOTS
MLR
BIVARIATE
SCATTER PLOTS
REGRESSION
RELATIONAL
COMPARATIVE
OUTLIERS
SYSTEMATIC DIFFERENCES
YES
VALUE IN ERROR
MODIFY OR DELETE VALUE
NO
YES
SYSTEMATIC ERROR
FLAG OR MODIFY VALUES
NO
DATA SET NO. 3
(VALIDATED)

Figure 9. Data validation process for the Eastern Lake Survey - Phase I.

SECTION 4

RESULTS

Evaluation of the quality assurance and quality control data was an ongoing process during and following the ELS-I. A substantial part of this evaluation process involved the statistical analysis of the QA and QC sample results which is presented below. Results of an independent statistical analysis of these data are included as Appendix A.

Evaluations were also made of the field and laboratory operations, the verification procedures, the analytical methods, and the chemical analyses of samples split between ELS-I analytical laboratories and ERL-Corvallis, Canadian, or Norwegian laboratories. These evaluations are summarized below.

OPERATIONS EVALUATION

Overall, operation of the ELS-I proceeded smoothly. The QA-QC program was strictly adhered to throughout the period of operations. Some specific problems were encountered as could be expected for a study of this magnitude. These problems were usually detected and quickly resolved. Some protocol changes were implemented during the survey; others were made after the survey as a result of debriefing and evaluation recommendations. All changes were incorporated into the final QA plan (Drousé et al. 1986) and were implemented during subsequent NSWS operations.

The ELS-I was completed in a timely manner, and data of known quality were collected consistently throughout the period of operations. The statistical requirements for adequate sample size were achieved at all field stations. There were no major interruptions in field operations due to accidents, weather, or equipment failure. The sampling and laboratory protocols were very successful for most procedures and should serve as a model for future field studies of a similar nature.

Lake and Sample Information

Field operations were a successful means for obtaining samples and field data consistent with the ELS-I research plan. Approximately 90 percent of the lakes initially selected for sampling were visited by sampling crews, and of those lakes visited, 96 percent (1,612) were actually sampled. In addition to those lakes, 186 special interest lakes were sampled for a total sample of 1,798 lakes. The numbers of regular lakes selected, visited, and sampled during the ELS-I are listed by subregion in Morris et al. (1986).

Less than 20 percent of the lakes visited were sampled at a depth other than the one originally specified. Only 5 percent of the lakes sampled were thermally stratified; thus, 95 percent of all samples were acceptable in terms of the research plan requirement that a single water sample was to be collected from each lake during a period when the lakes were isothermal. Five lakes were improperly located; data for these lakes were removed from the data base and the lakes were classified as 'not visited'.

In total, 2,389 routine, field duplicate, and field blank samples were delivered from the field laboratories to the contract analytical laboratories (Table 11). This resulted in 2,639 sets of analyses because the contract required that one matrix spike and one laboratory duplicate be analyzed per batch of samples. The distribution of samples by field station and analytical laboratory is provided in Table 12. Sample results are presented by region in Linthurst et al. (1986).

TABLE 11. NUMBERS OF LAKES SAMPLED, SAMPLES RECEIVED, AND SAMPLES ANALYZED BY CONTRACT LABORATORIES DURING THE EASTERN LAKE SURVEY - PHASE I

Laboratory	Lakes Sampled	Samples Received[a]	Samples Analyzed[b]
Versar	649	872	970
EMSI	752	983	1,081
Global	238	332	366
USGS-CO	159	202	222
Total	1,798	2,389	2,639

[a] Includes field duplicates, field blanks, and field and laboratory audits.
[b] Includes analysis of matrix spikes and laboratory duplicates (11% lab QC).

Field Problems and Resolutions

In general, the sampling teams performed as planned during the ELS-I with an average yield of 20 processed samples per operating day from each field laboratory. Three significant problems were identified and corrected during field operations. These concerned an inaccurate pH meter, contamination of blanks from one field laboratory, and destruction of one set of split samples. The identification of the problems and the corrective actions taken are discussed below.

Prior to the beginning of routine lake sampling from the Duluth and Rhinelander field stations, a practice sampling excursion was undertaken. Samples collected during that excursion were split between the Duluth and Rhinelander field laboratories for processing and chemical analyses. When the data were evaluated, it was found that the Duluth pH measurements differed from

TABLE 12. NUMBERS OF SAMPLES DELIVERED BY FIELD STATIONS DURING THE EASTERN LAKE SURVEY - PHASE I

	Analytical Laboratories				
Field Station	Versar	EMSI	Global	USGS-CO	Total
Bangor	--	213	--	--	213
Lexington	77	332	--	--	409
Lake Placid	--	332	--	--	332
Mt. Pocono	99	106	--	--	205
Duluth	343	--	54	--	397
Rhinelander	353	--	116	--	469
Asheville	--	--	162	--	162
Lakeland	--	--	--	202	202
Total Samples	872	983	332	202	2,389

the Rhinelander measurements by one pH unit at pH values greater than 6.0. Measurements of the buffers used for calibration and for the QCCS were found to be accurate. After changing the pH electrodes, checking the buffers, and reviewing the measurement technique, the problem was eventually traced to a faulty electronic display on the Duluth pH meter. A replacement meter was obtained and was used throughout the survey. The problem with the Duluth pH meter led to implementation of an additional, mid-level QC check at all field stations. For each batch of samples, the laboratory supervisor was required to compare the Hydrolab pH measurements with the field laboratory measurement and to take corrective action if the two values differed by more than 0.5 pH unit.

Some field blanks associated with the Lexington field station were found to have high levels of several major cations and anions. Further investigation revealed that, because of failure of the reverse osmosis-deionization (RO-DI) water system in the field laboratory, the field personnel had been instructed to take distilled water for two batches from the EPA regional laboratory still. Each field station was subsequently informed of the problem and was cautioned to use only field laboratory RO-DI water for field blanks.

No routine samples were lost during the ELS-I although one batch of samples was temporarily misrouted in shipment to the contract analytical laboratory. These samples were located by using the sample tracking procedures for the survey and were analyzed within the required sample holding time. The Norwegian split samples collected from Region 1E were inadvertently destroyed by the commercial courier service. A second set of split samples was collected from Region 3A for shipment to Norway.

Several general recommendations to improve field operations of future NSWS activities were obtained from summaries provided by each EPA base coordinator. Many of the temporary employees hired by Lockheed-EMSCO as field sampling and field laboratory personnel also provided debriefing letters before or shortly after the ELS-I was completed. In addition, all field laboratory notebooks were turned over to the QA manager. A debriefing was held for all EPA base coordinators and duty officers and members of the NSWS management team in Plant City, Florida, in December 1984. Topics from that meeting related to the quality assurance program included communications, sample shipment, and training. These topics are discussed below.

Efficient and complete information transfer between the NSWS management team and the field stations was necessary to ensure that all new developments or modifications in operational protocols were consistently disseminated and understood.

Shipment of samples to the contract analytical laboratories was a problem on weekends especially when there was no service by overnight courier. Weekend shipments using commercial airlines required close coordination between the field laboratory and contract laboratory personnel to assure that the samples were received at the contract laboratories within the appropriate time. The contract laboratories later suggested holding weekend shipments until Monday, since it was easier for them to meet the holding time constraints than to pick up samples at the airport.

More comprehensive instruction to field samplers in the completion of field data forms was recommended to ensure clarity and consistency. It was suggested that training at each field station be lengthened, since some field sampling personnel lacked experience and an understanding of limnology and certain types of sampling equipment. At some field stations, state or regional EPA sampling personnel were rotated and were replaced by new people on a frequent basis. It was suggested that this practice be discouraged if possible because it added to inconsistencies in data reporting and required that additional time and effort be spent on training activities.

Analytical Laboratory Problems and Resolutions

During the ELS-I, there was one occurrence of a sample volume overload at one analytical laboratory. This problem was immediately resolved by distributing some samples to another analytical laboratory.

Several analytical problems were identified and corrected during the survey operations. Two significant difficulties centered on the calibration method used with silica measurement at one laboratory and on aluminum contamination problems at three laboratories. These are discussed below.

The daily QA checks and audit sample data comparisons by the QA staff indicated that the silica results from one laboratory had a negative bias. Field blank data with highly negative values were also being reported by the same laboratory. The bias was eventually traced to a calibration problem. The other laboratories did not experience the same difficulty. The laboratory in error was calibrating for silica in the 10 to 60 ppm range which was specified for the method as obtained from the literature. However, the silica method as used in the survey also specified that the calibration standards bracket the expected sample concentrations which were well below the 10 to 60 ppm range. The laboratory involved calibrated its instruments for silica analyses from 0 to 10 ppm thereafter and reanalyzed the affected samples. Data from reanalysis for silica were thoroughly reviewed for technical merit before substitution into the raw data set.

During the pilot study, laboratory blank values were reported for total aluminum that were equal to or greater than the values found in routine samples. The high aluminum concentrations, believed to be caused by either airborne dust contamination, reagent and glassware contamination, or both, occurred at two laboratories. A major source of contamination was traced to the use of borosilicate glassware which contains aluminum oxide. During the digestion procedure, aluminum was being leached from the glass. Teflon beakers were substituted for glass in each laboratory.

The initial sample batches analyzed at one laboratory also exhibited sporadic aluminum contamination. Through the daily QA contact with this laboratory, the problem was identified and was quickly traced to a building maintenance operation. The floors in an adjacent room had been sanded during the weekend while several sample batches were being digested for measurement of total aluminum. As a result, all laboratories were instructed to improve contamination control procedures by performing digestions in a laminar-flow hood or in an isolated station within a standard fume hood to prevent airborne contamination. This procedure was implemented at all participating laboratories.

METHODS EVALUATION

Several analytical questions arose during the planning for the ELS-I; others arose as problems during the pilot studies. Methods studies were conducted at EMSL-LV to address and resolve these issues. Questions that arose during the planning stages included the practicality of measuring free dissolved fluoride, the relative merits of ion chromatography (IC) versus ion-selective electrodes (ISE) for measurement of total dissolved fluoride, and the accuracy of Gran analysis for determinations of ANC and BNC. These issues were evaluated during and following the pilot study. Other issues that were identified during the pilot study concerned the procedure for measuring total extractable aluminum, the design of the pH sample chamber, the effects of filtration on iron and aluminum in the audit samples, and nitrate contamination in blank samples. These methods evaluations are discussed below.

Fluoride Determinations

Prior to the start of the ELS-I, free dissolved fluoride was chosen as one of the parameters of interest. It is an important parameter to consider in modeling aluminum chemistry, but it is difficult to measure. No satisfactory method could be found in the literature, and none was recommended by the analytical experts at a workshop which was held in Denver, Colorado, during the planning stage of the ELS-I.

On a trial basis, a simple ion-selective electrode method was used during the pilot study. Pilot study results for free dissolved fluoride tended to be variable and often were higher than those for total dissolved fluoride. Also, the measurement was very time-consuming. Based on the pilot study results, free dissolved fluoride was dropped from the list of parameters for the NSWS until an acceptable method for the determination could be developed.

At the Denver analytical workshop, two methods were suggested for the determination of total dissolved fluoride: ion-selective electrode (ISE) and ion chromatography (IC). The ISE method is a standard analytical technique, but the electrode is characterized by low sensitivity and slow response especially when the fluoride concentration is below 0.1 mg L^{-1}. The IC method is not commonly used for fluoride determinations, but it is very sensitive (detection limit <0.005 mg L^{-1}), rapid (analysis time less than 8 minutes), and easily automated. It is also possible to simultaneously measure anions in addition to fluoride by using IC. However, the determination of fluoride by IC is subject to interferences such as the "water dip" and measurement of small organic species that elute at the same time as fluoride (Hillman et al. 1986). It was concluded that despite its advantages IC is not a suitable method for measuring total dissolved fluoride in natural waters under standard IC conditions. Total dissolved fluoride was therefore measured with ISE during the ELS-I.

Acid-Neutralizing Capacity and Base-Neutralizing Capacity

In order to maximize the accuracy and precision of ANC and BNC determinations, a full Gran analysis was specified for interpreting titration data. Because Gran analysis is not a standard technique for measuring ANC and BNC and because complex calculations were involved, several samples were analyzed prior to the ELS-I to ensure that the calculations were correct and to provide detailed examples to the analytical laboratories. These examples were included in both the IFB and the analytical methods manual. Technical difficulties were encountered with the interpretation of BNC titration data which are presently unresolved. This parameter is not discussed further in the present report.

Total Extractable Aluminum

Although the method specified for the determination of total extractable Al is based on methods in the literature (Barnes 1975; May et al. 1979), questions arose during the pilot study regarding the effects of sample filtration and filter type (brand and composition), sample temperature, and extraction technique. Estimates of precision based on both single- and multi-analyst measurements were desired. In order to obtain this information, a series of experiments was performed which made use of the natural audit sample from Big Moose Lake.

The effect of filter type on analytical results was examined by determining total extractable Al in an unfiltered sample and in three filtered samples; a different type of membrane filter was used for each sample. The analytical results indicated that neither filtration (0.45-μm pore size) nor filter type had an effect on total extractable Al concentrations. A Gelman 0.45-μm cellulose-nitrate membrane filter was selected for use during the ELS-I.

The question of sample temperature arose because an effort was not made during the pilot study to ensure that samples were at the same temperature prior to Al extraction. If sample temperature were important, then the comparability of results among lakes would be affected. To determine whether temperature had an effect on total extractable Al concentration, portions of a sample were equilibrated at two different temperatures (4°C and 20°C) and then extracted. The results of this experiment indicated that sample temperature had no effect on total extractable Al concentration.

The experimental protocol for total extractable Al called for a rapid extraction with 8-hydroxyquinoline into methyl isobutyl ketone (MIBK). Because the complexation time and the method for this extraction were not specified, it was necessary to estimate the effect of small variations in the extraction technique. Portions of the natural audit sample were extracted by using two mixing styles (vigorous shaking and no deliberate shaking after hydroxyquinoline addition) and two complexation times (5 seconds and 20 seconds). Equivalent results were obtained for each of the experiments; i.e., small variations in extraction technique did not affect the measured sample concentrations.

The lack of effect from variations in extraction technique was seen when determining single- and multi-analyst precision. The mean concentrations and standard deviations of total extractable Al measurements by a single analyst (0.192 ± 0.011 mg L^{-1}, n=24) and by several analysts (0.193 ± 0.010 mg L^{-1}, 11 analysts, 2 extractions each) are essentially identical. This experiment demonstrated that, with adequate personnel training, total extractable Al results were not affected by any among-analyst variations in extraction technique.

pH Sample Chamber

During the ELS-I, sealed syringe samples were obtained at each lake for pH determinations. Sealing samples in syringes was expected to preserve sample pH by minimizing exchange of dissolved CO_2 with the atmosphere. A sample chamber was also developed for the field laboratory pH measurements to prevent exposure of the sample to air (Hillman et al. 1986).

Formation of Filterable Iron and Aluminum Complexes in Synthetic Field Audit Samples

During the pilot study, concentrations of dissolved Fe and total extractable Al concentrations in field synthetic audit samples were consistently lower than those in laboratory synthetic audit samples. The primary difference between laboratory synthetic and field synthetic audit samples was that laboratory audits were processed (acidified for Fe analysis and extracted into MIBK for Al analysis) immediately after preparation without filtering, and field audits were processed (with filtration) 24 to 72 hours after preparation. The probable cause for lower concentrations of Fe and total extractable Al in the field audit samples was that, during the time delay between audit sample preparation and filtration (approximately 1 day), hydroxides or other complexes were formed that did not pass through the 0.45-µm membrane filter.

An experiment was performed to determine the cause of the low concentrations of Fe and total extractable Al in field audit samples. Three aliquots each from the low level and the high level field synthetic audit samples were acidified to pH <2 with analytical grade nitric acid and were analyzed for Fe and total extractable Al. Three additional aliquots from each audit sample were similarly prepared, except that they were analyzed after being filtered through a 0.45-μm membrane.

The analytical results suggested that total extractable Al was lost from the field audit samples during filtration. The purpose of sample filtration was to remove suspended materials which at pH 6 to 8 may have included hydroxyaluminum complexes. This explanation is consistent with the observation that laboratory audit sample values for total extractable Al were higher than field audit sample values. By extracting the laboratory audit samples immediately after preparation (within 1 hour), the formation of large polymeric Al species may have been avoided, and, hence, extractable Al was not lost from the samples.

Furthermore, Fe was not detected in either the filtered or the unfiltered field audit samples. In those samples, Fe probably formed a precipitate which was adsorbed to the sample bottle between the time of preparation at the audit sample support laboratory and the time of processing (filtration and acidification) in the field laboratory. Because the samples were filtered prior to being acidified, the adsorbed Fe precipitate would have been lost from these samples. In the laboratory audit samples which were processed by the audit sample support laboratory immediately after preparation, the precipitate may not have had time to form. Field audit results for Fe and total extractable Al were therefore not included in statistical evaluations.

Nitrate Contamination

To meet analytical laboratory quality control specifications, nitrate concentrations in field blank samples were required to be less than 0.01 mg L^{-1}. However, during the ELS-I pilot study, up to 18 mg L^{-1} nitrate was detected in field blanks, which suggested that a serious contamination problem existed. This contamination was not present in the analytical laboratory blank samples. After discussions with the managers of the contract laboratories performing the nitrate analyses, it was concluded that the source of the contamination was not in the contract laboratory but was in the cleaning procedure for aliquot 3 sample containers. That cleaning procedure which included a nitric acid rinse is outlined in Table 13. As a first attempt at eliminating the contamination, the nitric acid rinse was omitted from the cleaning procedure for aliquot 3 containers during the ELS-I.

Another potential source of contamination was the sample filtration procedure at the field laboratory which included a nitric acid rinse of the filter holder and membrane followed by copious rinsing with RO-DI water. This step was not considered to be a problem at the time that the bottle cleaning procedure was changed, and during the ELS-I field laboratory training sessions, the need for copious rinsing of the filtration apparatus was stressed.

The change in the cleaning procedure for the sample containers and the rinsing step in the filtration process reduced but did not eliminate the

TABLE 13. CLEANING PROCEDURE USED FOR ALIQUOT 3 SAMPLE CONTAINERS, DURING THE EASTERN LAKE SURVEY - PHASE I PILOT STUDY

1. Rinse container three times with deionized water.
2. Rinse container three times with 3 N HNO_3.
3. Rinse container six times with deionized water.
4. Fill container with deionized water and allow to stand for 48 hours.
5. Empty container, air dry in a laminar-flow hood (class 100 air).
6. Cap containers and place in clean plastic bags.

Note: Deionized water must meet ASTM specifications for Type I Reagent Water. Nitric acid is Baker Instra-Analyzed or equivalent.

nitrate contamination problem. Field blank samples obtained during the early part of the ELS-I still contained up to 3.5 mg L^{-1} nitrate. Overall, the mean nitrate concentration in field blank samples during the early part of the ELS-I was 0.3 ± 0.6 mg L^{-1} (n = 146). It became apparent that the filtration procedure was a source of more contamination than was previously expected.

In the original filtration procedure (Table 14), the filter holder and membrane were rinsed with 5 percent HNO_3 between samples. In a further attempt to eliminate the nitrate contamination, the nitric acid rinse was eliminated for aliquot 3. However, the same filtrator was still used for all aliquots, and the filtration procedure during the processing of aliquots 1 and 4 included a nitric acid rinse of the filter holders and membranes. Blanks processed in this manner still contained about 0.05 mg L^{-1} nitrate. Further investigation revealed that the design of the filter holder permitted intermittent nitrate contamination (i.e., nitrate was not completely removed by successive deionized water rinses). To avoid this occurrence, the filtration procedure for the ELS-I was modified to include the use of separate filter holders and membranes to obtain the unacidified aliquots. New filter holders were dedicated to the aliquot 3 filtration and were never allowed to contact nitric acid.

To determine whether the new filtration procedure eliminated nitrate contamination of aliquot 3, a series of experiments was performed at the field laboratories in Duluth, Lexington, and Rhinelander. At each laboratory, 10 4-liter deionized water samples (2 samples every hour for 5 hours) were collected and processed, each in three different ways (Table 15) at the times and dates of sample preparation given in Table 16. The processed samples were then analyzed for nitrate at EMSL-LV. The Lexington samples were also split between EMSL-LV and Western Washington University (WWU) for analysis. Detection limits for nitrate at EMSL-LV and WWU were 0.001 and 0.002 mg L^{-1}, respectively.

A comparison of the nitrate data from EMSL-LV and WWU is given in Table 17. The data from EMSL-LV indicate that the nitrate concentrations in deionized water used to prepare the field laboratory blank samples were 0.005 mg L^{-1} or less in 28 of 30 samples. The two exceptions (both at Duluth) had concentrations less than or equal to 0.01 mg L^{-1} nitrate. With one exception, the nitrate concentration in samples prepared by process 3 (filtered sample, filter

TABLE 14. FILTRATION PROCEDURE ORIGINALLY USED BY FIELD PERSONNEL DURING THE EASTERN LAKE SURVEY - PHASE I

Filtered Aliquots - Filtered sample is obtained by vacuum filtration through a 0.45-µm membrane filter into a clean 500-mL container. The filtered sample is then transferred into the containers for aliquots 1, 3, and 4. The filtration is performed as follows:

a. Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter in succession with 20 to 40 mL of deionized water, 20 mL of 5% HNO_3 (Baker Instra-Analyzed grade), and 40 to 50 mL of deionized water (it is CRUCIAL that all traces of the HNO_3 rinse be removed).

b. Rinse the filter holder and membrane with 10 to 15 mL of the sample to be filtered.

c. Replace the waste container with a clean 500-mL plastic bottle. Reapply vacuum (vacuum pressure must not exceed 12 inches Hg), and filter 10 to 15 mL of sample into the bottle. Rinse the container by slowly rotating the bottle so that the sample touches all surfaces. Discard the rinse and place the 500-mL bottle back under the filter holder.

d. Filter the sample into the 500-mL bottle until the bottle is full.

e. Transfer filtered sample into aliquot containers 1, 3, and 4 (previously labeled) after first rinsing containers with 10 to 15 mL of filtered sample (as described in "c").

f. If necessary, return the 500-mL bottle to the filtration apparatus and collect additional filtered sample [about 700 mL of filtered sample is required for aliquots 1 (250 mL), 3 (250 mL), and 4 (125 mL)].

holder rinsed with deionized water only) was 0.005 mg L^{-1} or less. That exception (Duluth 5) contained less than 0.02 mg L^{-1} nitrate.

Both the WWU and EMSL-LV data indicated that process 2 (filtered sample, filter holder rinsed with HNO_3, then with deionized water) produced field laboratory blank samples with high concentrations of nitrate (values ranging from 0.004 to 1.650 mg L^{-1} with an average of 0.2 ± 0.5 mg L^{-1}). Again, field blank samples filtered using process 3 contained low concentrations of nitrate. WWU reported no nitrate values above their instrumental detection limit (0.002 mg L^{-1} nitrate) when process 3 was used.

By making a comparison of the results using process 2 with those using process 3, it was concluded that the nitric acid rinse of filter holders and filter membranes was responsible for the nitrate contamination seen in field blanks (and, by implication, in routine and duplicate samples). By using

TABLE 15. FIELD LABORATORY FILTRATION PROCEDURES USED IN THE NITRATE CONTAMINATION EXPERIMENT DURING THE EASTERN LAKE SURVEY - PHASE I

Process 1.	(Raw, unfiltered sample - no treatment.)
	a. Rinse two aliquot 3 bottles with sample (4-liter deionized water) and discard rinse water.
	b. Fill with fresh sample and seal.
	c. Label samples as A and B.
Process 2.[a]	(Filtered sample, filter holder rinsed with acid and then with deionized water.)
	a. Assemble filtration apparatus, rinse once with 5% nitric acid, followed by three deionized water rinses.
	b. Insert filter membrane, rinse once with nitric acid and follow with three deionized water rinses.
	c. Filter 300 to 400 mL deionized water sample into waste container.
	d. Replace filter membrane with new membrane. Rinse three times with deionized water and once with 20 mL sample.
	e. Place clean aliquot 5 bottle (500 mL) under filter holder. Filter 20 mL sample into bottle. Rinse bottle with this initial portion, then discard rinse. Filter and collect 500 mL of sample.
	f. Transfer filtered sample to two aliquot 3 bottles. Label as C and D.
Process 3.	(Filtered sample, filter holder rinsed with deionized water only.)
	a. Assemble filtration apparatus using a new filter holder. Rinse three times with deionized water.
	b. Insert filter membrane. Rinse three times with deionized water and follow with one 20-mL rinse with sample.
	c. Place a clean aliquot 5 bottle (500 mL) under filter holder. Filter 20 mL sample into bottle. Rinse bottle with this initial portion, then discard rinse. Filter and collect 500 mL sample.
	d. Transfer filtered sample to two aliquot 3 bottles. Label as E and F.

[a] Step d of process 2 performed at Duluth field station only.

TABLE 16. DESCRIPTION OF FIELD LABORATORY BLANK SAMPLES COLLECTED IN THE NITRATE CONTAMINATION EXPERIMENT DURING THE EASTERN LAKE SURVEY - PHASE I

	Dates[a] and Times[b] of Sample Processing		
Sample	Lexington[c]	Rhinelander[c]	Duluth[d]
1	10/28/84,1000	10/29/84,1325	10/28/84
2	10/28/84,1000	10/29/84,1330	10/28/84
3	10/28/84,1100	10/29/84,1420	10/28/84
4	10/28/84,1100	10/29/84,1420	10/28/84
5	10/28/84,1200	10/29/84,1530	10/28/84
6	10/28/84,1200	10/29/84,1530	10/28/84
7	10/28/84,1300	10/29/84,1630	10/28/84
8	10/28/84,1300	10/29/84,1630	10/28/84
9	10/28/84,1400	10/29/84,0900	10/28/84
10	10/28/84,1400	10/29/84,0900	10/28/84
11[e]	10/28/84,1400	--	--
12[f]	10/28/84,1400	--	--

[a] Day the sample was collected and processed (filtered).

[b] Time the water sample was collected from the Millipore system.

[c] Times and dates of sample collection. All samples were processed on 10/30/84.

[d] Time unknown.

[e] This sample was taken from the still in the EPA regional lab in Lexington, Massachusetts.

[f] This sample was taken from the deionized water spigot in the EPA regional lab in Lexington, Massachusetts.

process 3 to prepare aliquot 3, nitrate concentrations in field blanks were reduced to levels less than 0.01 mg L^{-1} for the remainder of the ELS-I.

It should be noted that the sources of contamination can be traced to the deionized water, sample containers, and filtration apparatus, which contributed up to 1.65 mg L^{-1} of nitrate to field laboratory blank samples in this experiment. Two raw unfiltered samples (Duluth 8-1 and 9-1) contained 0.009 and 0.010 mg L^{-1} nitrate, respectively, and the two corresponding filtered samples (deionized water only, Duluth 8-3 and 9-3) contained 0.003 and 0.005 mg L^{-1} nitrate. The aliquot bottles (rather than the deionized water) were the most likely source of the slight contamination in Duluth samples 8-1 and 9-1. Similarly, a raw unfiltered sample (Duluth 5-1) contained 0.005 mg L^{-1} nitrate while a corresponding filtered aliquot (deionized water only, Duluth 5-3) contained 0.018 mg L^{-1} nitrate. In this case, the contamination was probably from either the aliquot bottle or the filtration apparatus. Both of these examples indicate the extreme care that was necessary to reduce nitrate contamination to less than 0.005 mg L^{-1}. The ELS was about halfway completed (November 1, 1984) before the cause of nitrate contamination was isolated and corrected. The QA manager immediately asked the contract laboratories to reanalyze nitrate in aliquot 5, the unfiltered aliquot. Unfortunately, most

TABLE 17. NITRATE CONCENTRATIONS IN FIELD LABORATORY BLANK SAMPLES FROM THE NITRATE CONTAMINATION EXPERIMENT, EASTERN LAKE SURVEY - PHASE I

		NO_3^- (mg L^{-1})[a]			
Sample	Process	Duluth EMSL-LV	Rhinelander EMSL-LV	Lexington EMSL-LV	Lexington WWU
1	1	0.003	0.003	0.001	ND[b]
2	1	0.005	0.003	0.001	ND
3	1	0.005	0.003	0.001	ND
4	1	0.005	0.003	0.001	ND
5	1	0.005	0.003	0.001	ND
6	1	0.003	0.003	0.001	ND
7	1	0.003	0.003	0.001	--
8	1	0.009, 0.009	0.003	0.005	ND
9	1	0.010	0.003	0.001	ND
10	1	0.003	0.003	0.005	ND
11	1	--	--	0.044	--
12	1	--	--	0.001	0.046, 0.046
1	2	0.033	0.006	0.042	0.077
2	2	0.033	0.014	1.130	1.650
3	2	0.033	0.006	0.146	0.128
4	2	0.036	0.008, 0.007	0.046	0.062
5	2	0.059	0.013	0.044	0.046
6	2	0.224	0.023	0.088	0.126
7	2	0.051	0.015	0.104	0.108
8	2	0.033, 0.035	0.186	0.025	0.032
9	2	0.020	0.006	0.023	0.030
10	2	0.171	0.006	0.008	0.004
1	3	0.005	0.003	0.001	ND
2	3	0.005	0.003	0.001	ND
3	3	0.003	0.003	0.001	ND
4	3	0.003	0.003	0.001	ND
5	3	0.018	0.003	0.001	ND
6	3	0.005	0.003	0.001	ND
7	3	0.003	0.002	0.001	ND
8	3	0.003	0.003	0.001	ND
9	3	0.005	0.003	0.001	ND
10	3	0.002	0.003	0.001	ND

[a] All samples were analyzed within 7 days of preparation.

[b] ND = not detected (less than 0.002 mg L^{-1} NO_3^-).

aliquot 5 nitrate determinations were performed well outside the maximum allowable holding time of seven days. After extensive statistical review, it was decided to replace all nitrate data processed on or before November 1, 1984, with the aliquot 5 data.

Evaluation of Split Sample Analyses from Norway and Canada

A study was undertaken to determine whether the analytical methods that were used in the ELS-I are comparable to the methods used in other regions where surface water surveys are conducted. In this study, 110 identical aliquots (split samples) from 97 lakes in the southern Blue Ridge Mountains (NSWS subregion 3A) were shipped to the Norwegian Institute for Water Research in Oslo, Norway, and to Global Geochemical Corporation in Canoga Park, California. The split samples were analyzed for 11 chemical parameters (pH, Ca, Mg, Na, K, conductance, NO_3^-, Cl^-, labile Al, SO_4^{2-}, and ANC) at each of these laboratories (Table 18).

In addition, 105 split samples from 92 lakes in the Adirondack Mountains (NSWS subregion 1A) were shipped to the Water Quality National Laboratory of the Canada Center for Inland Waters (CCIW) in Burlington, Ontario, to the Water Quality Section of the Ontario Ministry of the Environment (MOE) in Rexdale, Ontario, and to Environmental Monitoring and Services, Incorporated (EMSI) in Thousand Oaks, California. These split samples were analyzed for 18 parameters at EMSI and at the Canadian laboratories (pH, Cl^-, NO_3^-, Ca, conductance, SiO_2, DOC, DIC, Na, K, Mg, SO_4^{2-}, and ANC at CCIW; total P, total dissolved F^-, total Al, Fe, and Mn at MOE). Nitrate data were not compared because of analytical problems at the Canadian laboratory.

Linear regressions and sign tests were used to evaluate the comparability of the measurements from different laboratories. The linear regressions were performed twice for each comparison by alternately using each of the laboratories as the independent variable. The regression coefficient (r^2) was used to assess the overall adequacy of the linear model, and the slope and the y-intercept of the regression equation were used to describe the degree and the type of bias between the measurements. A concentration-dependent bias between the measurements from different laboratories is indicated when the slope is different from 1.00. A uniform (concentration-independent) bias between the sample measurements is indicated when the y-intercept is different from 0.00 and the slope is equal to 1.00. There is no bias when the slope is equal to 1.00 and the y-intercept is equal to 0.00; i.e., the measurements from the two laboratories are equivalent. The methods that were used for sample handling and analysis and for the statistical evaluations in this study are described in greater detail in M. A. Stapanian et al. (in preparation).

At the 90 percent confidence level, differences in 10 of the 11 parameters measured by the Norwegian and the ELS-I laboratories are well described by the linear model, regardless of which laboratory is the independent variable (Table 19). The labile Al measurements are not well described by the linear model at the 90 percent confidence level, regardless of which laboratory is the independent variable. A concentration-dependent bias (slope different from 1.00) is indicated between the Norwegian and the ELS-I measurements for Ca, Mg, Na, SO_4^{2-}, and conductance, regardless of which laboratory is the independent variable (see Table 19). A concentration-dependent bias is also indicated for

TABLE 18. CHEMICAL PARAMETERS MEASURED AND ANALYTICAL METHODS USED IN THE INTERCOMPARISON STUDY DURING THE EASTERN LAKE SURVEY - PHASE I

Parameters	Method of Analysis[a]		
	ELS-I	Canadian	Norwegian
Al, labile ($mg\ L^{-1}$)	AAS-furnace	not compared	PCV (total reactive)
Al, total ($mg\ L^{-1}$)	AAS-furnace	ICPES	not compared
ANC ($\mu eq\ L^{-1}$)	Gran analysis	Gran analysis	fixed-endpoint
Ca ($mg\ L^{-1}$)	AAS-flame	AAS-flame	AAS-flame
Cl^- ($mg\ L^{-1}$)	IC	IC	AC
Conductance ($\mu S\ cm^{-1}$)	Conductivity meter	Conductivity meter	Conductivity meter
DIC, air-equilibrated ($mg\ L^{-1}$)	Carbon analyzer	Carbon analyzer	not compared
DOC ($mg\ L^{-1}$)	Carbon analyzer	Carbon analyzer	not compared
F^-, total dissolved ($mg\ L^{-1}$)	ISE	ISE	not compared
Fe ($mg\ L^{-1}$)	AAS-flame	ICPES	not compared
K ($mg\ L^{-1}$)	AAS-flame	flame photometry	AAS-flame
Mg ($mg\ L^{-1}$)	AAS-flame	AAS-flame	AAS-flame
Mn ($mg\ L^{-1}$)	AAS-flame	ICPES	not compared
Na ($mg\ L^{-1}$)	AAS-flame	flame photometry	AAS-flame
NO_3^- ($mg\ L^{-1}$)	IC	not compared	AC
P, total ($mg\ L^{-1}$)	AC	AC	not compared
pH	pH meter	pH meter	pH meter
SiO_2 ($mg\ L^{-1}$)	AC	AC	not compared
SO_4^{2-} ($mg\ L^{-1}$)	IC	IC	AC

[a] Method references are given in U.S. Stapanian et al. (in preparation). ICPES = inductively coupled plasma emission spectroscopy, AAS = atomic absorption spectroscopy, AC = automated colorimetry, PCV = pyrochatechol violet, ISE = ion selective electrode, IC = ion chromatography.

TABLE 19. RESULTS OF SIGN TESTS AND TWO LINEAR REGRESSIONS FOR EACH PARAMETER MEASURED IN THE NORWEIGAN AND ELS-I SPLIT SAMPLES

		Linear Regression[a]			
Parameter	n	Slope (SE)[b]	y-intercept (SE)[b]	r^2	Sign Test
Al, labile	105	0.332 (0.044)[c]	0.001 (0.000)[c]	0.361	ELS > Norway[c]
	108	0.835 (0.127)[d]	0.001 (0.000)[e]	0.291	
ANC	109	1.003 (0.003)[d]	-9.39 (0.975)[c]	0.999	ELS > Norway[c]
	109	0.996 (0.003)[d]	9.60 (0.950)[c]	0.999	
Ca	106	1.050 (0.007)[c]	0.098 (0.028)[c]	0.995	ELS < Norway[c]
	106	0.948 (0.007)[c]	-0.080 (0.027)[c]	0.995	
Cl^-	107	1.012 (0.017)[d]	-0.201 (0.043)[c]	0.970	ELS > Norway[c]
	110	0.866 (0.004)[c]	0.439 (0.044)[c]	0.998	
Conductance	109	0.981 (0.002)[c]	1.616 (0.139)[c]	1.000	ELS < Norway[c]
	109	-1.627 (0.144)[c]	1.019 (0.002)[c]	0.999	
K	107	1.000 (0.11)[d]	-0.041 (0.015)[c]	0.986	ELS > Norway[c]
	107	0.986 (0.11)[d]	0.056 (0.015)[c]	0.986	
Mg	108	1.035 (0.008)[c]	0.005 (0.008)[d]	0.994	ELS < Norway[c]
	108	0.961 (0.007)[c]	-0.000 (0.008)[d]	0.994	
Na	106	1.091 (0.003)[c]	-0.130 (0.020)[c]	0.999	ELS = Norway
	106	0.915 (0.003)[c]	0.122 (0.018)[c]	0.999	
NO_3^-	110	1.008 (0.007)[d]	-0.017 (0.008)[e]	0.994	ELS = Norway
	109	0.986 (0.005)[e]	0.015 (0.006)[e]	0.997	
pH	108	0.875 (0.023)[d]	0.759 (0.158)[c]	0.933	ELS > Norway[c]
	108	1.067 (0.028)[e]	-0.347 (0.190)[d]	0.933	
SO_4^{2-}	108	1.102 (0.009)[c]	-0.156 (0.029)[c]	0.992	ELS = Norway
	109	0.898 (0.005)[c]	0.161 (0.022)[c]	0.997	

[a] The ELS-I laboratory was designated as the independent variable in the first regression, and the Norwegian laboratory was designated as the independent variable in the second regression.

[b] For each parameter measured, the slope and intercept represent the linear model that yielded the higher value of r^2 when outliers (observations that had studentized residuals >3.0) were removed or when outliers were included. SE = standard error.

[c] Significant at $p < 0.01$.

[d] Not significant

[e] Significant at $p < 0.05$.

the labile Al measurements when the ELS-I laboratory is the independent variable and for the Cl^-, NO_3^-, and pH measurements when the Norwegian laboratory is the independent variable. The ANC and K measurements exhibit a uniform bias (slopes different from 1.00 and y-intercepts equal to 0.00).

On the basis of the sign test results, the set of ELS-I values is higher than the set of Norwegian values for labile Al, Cl^-, K, pH, and ANC (see Table 19). The set of Norwegian values is higher than the set of ELS-I values for Ca, Mg, and conductance, and there is no significant difference between the two sets of values for Na, NO_3^-, and SO_4^{2-}.

Regardless of which laboratory is used as the independent variable, differences between the ELS-I and Canadian measurements are well described by a linear model at the 90 percent confidence level for 14 of the 17 parameters (Table 20). Differences between the ELS-I and the Canadian measurements of Fe, Mn, and total P are not well described at the 90 percent confidence level. At the 95 percent confidence level, differences between the laboratories for 10 of the 17 measurements are well described by the linear model, regardless of which laboratory is the independent variable. The values of r^2 change slightly for Cl^-, Fe, Mn, and pH depending on which laboratory is the independent variable.

A concentration-dependent laboratory bias (slope different from 1.00) is indicated for the measurements of total Al, DOC, total dissolved F^-, Na, Mg, K, SiO_2, Fe, Mn, and pH regardless of which laboratory is the independent variable. A concentration-dependent bias also is indicated for SO_4^{2-} and for total P when the Canadian laboratory is the independent variable and for Cl^- when the ELS-I laboratory is the independent variable. The measurements of Ca, air-equilibrated DIC, and ANC show a uniform laboratory bias (slopes equal to 1.00 and y-intercepts different from 0.00) regardless of which laboratory is the independent variable. The conductance measurements show no laboratory bias (slopes equal to 1.00 and y-intercepts equal to 0.00) regardless of which laboratory is the independent variable.

On the basis of the sign test results, the ELS-I values are greater than the Canadian values for total Al, SO_4^{2-}, DOC, Cl^-, total P, ANC, Na, Mg, K, SiO_2, and pH (see Table 20). The Canadian values are greater than the ELS-I values for Ca, air-equilibrated DIC, Fe, and Mn; there is no significant difference between the two sets of values for conductance or for total dissolved F^-.

In summary, the measurements from the two pairs of laboratories are comparable for most of the parameters as indicated by the high values of the regression coefficients ($r^2 > 0.95$ for 38 of 56 comparisons and $r^2 > 0.90$ for 48 of 56 comparisons). The linear regression analysis also indicates that there are significant differences (uniform bias or concentration-dependent bias) between the ELS-I and Norwegian measurements and between the ELS-I and Canadian measurements for nearly all of the parameters.

The sign test shows that the set of ELS-I values is greater than the set of Norwegian values for 5 of the 11 parameters and it is less than the set of Norwegian values for 3 of the parameters; there is no significant difference between the 2 sets of values for the remaining 3 parameters. The set of ELS-I values is greater than the set of Canadian values for 11 of the 17 parameters

TABLE 20. RESULTS OF SIGN TESTS AND TWO LINEAR REGRESSIONS FOR EACH PARAMETER MEASURED IN THE CANADIAN AND ELS-I SPLIT SAMPLES

		Linear regression^{a}			
Parameter	n	Slope (SE)^{b}	y-intercept (SE)^{b}	r^2	Sign Test
Al, total	104	0.731 (0.024)^{c}	-0.015 (0.005)^{c}	0.901	ELS > Canada^{c}
	104	1.232 (0.040)^{c}	0.034 (0.006)^{c}	0.901	
ANC	102	0.999 (0.002)^{d}	-14.311 (1.088)^{c}	0.999	ELS > Canada^{c}
	102	1.001 (0.002)^{d}	14.440 (1.073)^{c}	0.999	
Ca	103	0.988 (0.004)^{d}	0.212 (0.030)^{c}	0.998	ELS < Canada^{c}
	103	1.010 (0.031)^{d}	-0.227 (0.036)^{c}	0.998	
Cl^-	101	0.718 (0.024)^{c}	0.137 (0.035)^{c}	0.897	ELS > Canada^{e}
	103	1.068 (0.035)^{d}	0.023 (0.054)^{d}	0.902	
Conductance	104	1.000 (0.000)^{d}	0.000 (0.000)^{d}	01.000	ELS = Canada
	104	1.000 (0.000)^{d}	0.000 (0.000)^{d}	01.000	
DIC, air-equilibrated	101	1.008 (0.007)^{d}	0.312 (0.031)^{c}	0.996	ELS < Canada^{c}
	101	0.992 (0.007)^{d}	0.081 (0.034)^{e}	0.996	
DOC	102	0.871 (0.014)^{c}	0.013 (0.059)^{d}	0.976	ELS > Canada^{c}
	102	1.121 (0.018)^{c}	0.077 (0.066)^{d}	0.976	
F^-, total dissolved	102	1.052 (0.016)^{c}	0.002 (0.001)^{e}	0.977	ELS = Canada
	102	0.929 (0.014)^{c}	0.003 (0.001)^{e}	0.977	
Fe	103	1.260 (0.091)^{c}	0.042 (0.008)^{c}	0.654	ELS < Canada^{c}
	102	0.453 (0.035)^{c}	0.002 (0.005)^{d}	0.631	
K	104	0.916 (0.004)^{c}	-0.006 (0.002)^{c}	0.998	ELS > Canada^{e}
	104	1.089 (0.005)^{c}	0.007 (0.002)^{c}	0.998	
Mg	102	0.939 (0.003)^{c}	0.023 (0.003)^{c}	0.999	ELS > Canada^{e}
	102	1.063 (0.003)^{c}	-0.024 (0.005)^{c}	0.999	
Mn	105	1.143 (0.057)^{c}	0.002 (0.002)^{d}	0.797	ELS < Canada^{c}
	104	0.759 (0.032)^{c}	0.002 (0.001)^{d}	0.849	
Na	103	0.971 (0.002)^{c}	-0.008 (0.003)^{e}	0.999	ELS > Canada^{e}
	103	1.029 (0.002)^{c}	0.008 (0.003)^{e}	0.999	
P, total	102	0.910 (0.108)^{d}	-0.001 (0.001)^{d}	0.417	ELS > Canada^{c}
	102	0.458 (0.054)^{c}	0.004 (0.000)^{c}	0.417	
pH	102	0.794 (0.025)^{c}	1.16 (0.154)^{c}	0.911	ELS > Canada^{c}
	104	1.093 (0.036)^{c}	-0.429 (0.221)^{d}	0.898	
SiO_2	103	0.926 (0.006)^{c}	0.052 (0.015)^{c}	0.996	ELS > Canada^{c}
	102	1.067 (0.007)^{c}	-0.039 (0.015)^{e}	0.996	
SO_4^{2-}	102	0.934 (0.032)^{e}	0.176 (0.180)^{d}	0.895	ELS > Canada^{e}
	102	0.958 (0.033)^{d}	0.387 (0.179)^{e}	0.895	

and it is less than the set of Canadian values for 4 of the parameters; there is no significant difference between the 2 sets of values for the remaining 2 parameters.

The components of overall variability in the split sample data may include random error (measurement imprecision) and systematic error (accuracy and specificity of the method). Measurement imprecision and differences in sample composition over time may contribute to the overall variability for all of the parameters measured by the ELS-I, Norwegian, and Canadian laboratories. Differences in analytical methodology may be expected to contribute to the overall variability of the ANC, labile Al, and NO_3^- data between the ELS-I and Norwegian laboratories. Differences between the methods used by the ELS-I and Canadian laboratories for Fe, K, Mn, Na, and total Al measurements also may be expected to contribute to the overall data variability.

ANC and Al are important parameters used for assessing the acidification of natural waters. The individual components of overall variability are statistically confounded for the ANC and Al measurements, but the possible influences on these data can be described. The negative y-intercepts in the ANC comparisons could be related to decreased ANC in the Norwegian and the Canadian split samples. One mechanism for this decrease is the cessation of photosynthetic activity (CO_2 fixation) in the samples during the holding time which could have resulted in $CaCO_3$ precipitation. The analytical methodology also differed between the ELS-I and Norwegian ANC measurements (see Table 18). For samples with low ANC, the fixed-endpoint titration has been reported to underestimate this parameter consistently when compared to the Gran analysis (Stumm and Morgan, 1981; Butler, 1982).

The slightly negative y-intercept is probably due to the inability of ICPES to detect the extremely low levels of total Al in the samples (Hanson and Ediger, 1980). The instrumental detection limit determined by LEMSCo for ICPES measurements of total Al is 0.043 mg L^{-1} (T. E. Lewis, pers. comm.). In this study, 52 of the 105 Canadian split samples had total Al concentrations ≤ 0.043 mg L^{-1} as measured by ICPES. For furnace AAS measurements of total Al by EMSI in the ELS-I, the reported and estimated instrumental detection limits are 0.002 and 0.006 mg L^{-1}, respectively (see Appendix B). In the intercomparison study, 2 of the 105 EMSI split samples measured by furnace AAS had total Al concentrations ≤ 0.002 mg L^{-1} and 5 samples had concentrations ≤ 0.006 mg L^{-1}. A linear regression analysis was performed to compare total Al values >0.043 mg L^{-1} from the Canadian laboratory with those from the ELS-I laboratory. The regression ($r^2 = 0.86$, n=53) yielded the following equation:

$$Al_{total}\ [Canada] = 0.71\ (Al_{total}\ [ELS\text{-}I]) - 0.005$$

The slope is significantly different from 1.00 ($p < 0.0001$) and the y-intercept is not significantly different from 0.00 at $p = 0.05$. The equation indicates a concentration-dependent bias with the ICPES (Canadian) measurements tending to be less than the corresponding furnace AAS (ELS-I) measurements. The precision of the 53 pairs of measurements is 53 percent, calculated as the root mean square of the percent relative standard deviation (RMS of % RSD). This precision value is close to the overall within-batch precision of 35 percent that is observed for 125 measurements of total Al across all ELS-I laboratories (see

Table 20). At higher concentrations (furnace AAS values > 0.35 mg L^{-1}), the precision (%RSD) values for the measurement pairs are generally less than 25 percent.

The source of the bias cannot be determined from these data because no synthetic audit samples or reference samples were analyzed as part of the comparison. The comparability between the two measurements is good, although the values are not identical. Additional study of the quantitative relationships between ICPES and furnace AAS measurements of total Al at higher concentrations is needed, based on the results of these comparisons.

EVALUATION OF DATA BASE QUALITY

Data Verification

In the ELS-I, several instances of misreported data were uncovered through daily QA checks and the data verification process. Although uncommon, errors were identified and traced to data transcription errors, switched aliquots in the field laboratory, mislabeled samples, and data entry errors at the ORNL data center. Through careful QA evaluation and follow-up with all participants, the incidents were identified and corrected.

As discussed in Section 3, general problems existed with the system used for modifying the ORNL raw data base. The system was slow; the entire cycle took about 10 days. A second system was implemented for a short time which was faster (3 days) but which required manual entry error checking and thus, was labor-intensive. The modification procedure has since been redesigned to facilitate error detection and data tracking while improving turn-around time.

Less than 3 percent of the raw data reported for lake samples was classified as reporting errors and was corrected before transfer to the verified data set. Sample reanalysis was requested for less than 4 percent of the originally reported raw data values. Less than 1 percent of the reported data required correction because of transcription or data entry errors. The overall error rate for data entry and updating of the raw data set to the verified data set was estimated by Lockheed-EMSCo QA personnel to be less than 0.03 percent.

Data Base Review

An independent review of the ELS-I data base was conducted to determine the adequacy of documentation of value changes, the correctness of data entry, the completeness of the data base, and the correctness of the calculations of population estimates (see Section 3). The results of this review indicated that all, or almost all, of the value changes are documented; that there are few if any data entry errors; that the data base is essentially complete; and that the calculations of population estimates are correct.

The documentation provided by the LEMSCo QA staff showed that the total number of numerical observations varies among the four data sets because QA and QC values were successively removed from the data base. The total number of data qualifiers (tags and flags) also varies among the different data sets. Qualifiers were added to the data base to explain the value changes and the discrepancies from expected values, and qualifiers were removed when questionable values were confirmed as being correct.

During the development of the validated and final data sets, two parameters (mineral acidity and carbonate alkalinity) were removed from the data base and some derived parameters (e.g., cation and anion sums) were added to the data base.

Approximately two percent of the routine and field duplicate values in the ELS-I data base were changed during the data verification process to correct reporting errors and data entry errors and to substitute values from chemical reanalyses. These changes were coordinated and documented by the LEMSCo QA staff. During the data validation process at ERL-C, approximately 100 data outliers were replaced with values obtained by averaging the routine and field duplicate values or by regression on other parameters. The numerical values for some parameters also were changed during data validation because of unit changes (e.g., mg L^{-1} to μeq L^{-1}) and all of the impossible negative values were changed to zero.

After the data were validated, most of the remaining field duplicate values were averaged with the corresponding routine sample values for each parameter to provide one set of values for each lake in the final data set. For 174 cases, the routine and field duplicate data were combined by using other arithmetic calculations. These alternate calculations were used when one of the raw values was discarded and the other was used for the final value, when values were affected by nitrate reanalyses, or when the averaged value was negative. The data base reviewers concluded that the value changes are well documented, and therefore the changes represent a considerable improvement in the overall quality of the ELS-I data base.

The data entry process was determined by the reviewers to be adequate because no discrepancies were found between the 300 rekeyed values and the corresponding values in the raw data set. If it is assumed that data entry errors occur at the same rate and independently across parameters, no errors out of 300 entries yields an overall error rate of less than or equal to 1 percent with 95 percent confidence for the 1800 lakes. The overall number of data entry and transcription errors was also estimated by the LEMSCo QA staff to be less than 1 percent.

The data base was essentially complete as determined by an examination of the data qualifiers for the missing value codes. There are approximately 250,000 routine and field duplicate values in the ELS-I data base, including nearly 20,000 (8 percent) missing value codes. Most of the missing value codes are correctly used for field data (Form 1) to indicate that the lake characteristics do not allow a measurement (e.g., inlet and outlet values for a seepage lake). In this data base there are no missing value codes for any of the primary or secondary variables (Linthurst et al. 1986), because the validation process called for the substitution of missing values with averages or with estimates by regression on values for other parameters.

The reviewers concluded that values for all parameters are available for almost every lake, and that the amount of ancillary information that is missing should not affect any foreseeable use of the data.

The computation of the population estimates was also verified by the data base reviewers. Because the recalculated estimates from a subset of the final data set agree with the ORNL population estimates to within four significant figures, the reviewers concluded that the population estimates are correctly calculated as prescribed by the data analysis plan for the ELS-I.

EVALUATION OF QUALITY ASSURANCE DATA

The QA program used a combination of blanks, duplicates, and audit samples to provide an external check on the quality of the ELS-I data and to allow early detection of problems in sample collection and analysis. Analytical data and associated QA and QC information were collected to define the overall and analytical within-batch precision and the overall and analytical among-batch precision for each parameter, the normal background contamination that occurred during the sampling and analytical process, and where possible, the bias among the laboratories that performed the analyses. This section presents a summary of the QA results.

Permutt and Pollack (1986) provided an additional statistical evaluation of the ELS-I data; their evaluation is included in this report as Appendix A. A summary of the report by Permutt and Pollack is provided at the end of this section with a review of their evaluation.

Blank Data

Both field blanks and analytical laboratory (calibration or reagent) blanks were analyzed during the ELS-I. Field blanks were analyzed for turbidity at the field laboratory and for 21 physicochemical parameters at the contract analytical laboratory. The contract laboratories used calibration and reagent blanks to control their background levels and to calculate their instrumental detection limits. These were reported weekly for each parameter except pH, conductance, ANC, and BNC.

Internal laboratory blanks were not routinely analyzed at the field laboratories because the limited number of analyses performed there would not have provided sufficient QA-QC information to justify the extra effort and expense. There were few problems achieving detection limits for measurements made in the field laboratories. In addition, pH and DIC measurements are highly variable in blank samples because of the tendency of blanks to absorb CO_2 from the air.

In total, 245 field blanks were collected during the ELS-I. The data were analyzed to provide an overall estimate of the normal background contamination that occurred during sampling and analysis and to identify and correct any significant contamination problems as they occurred. A statistical evaluation of the verified field blank data yielded a system decision limit and a system detection limit for each variable. The system decision limit represents the lowest instrument signal that can be distinguished from background at $\alpha = 0.05$.

The system detection limit is based on the reproducibility of the field blank analysis; it represents the lowest concentration that can be measured above the system decision limit.

The estimated instrumental detection limit was calculated from the reported calibration blank data. It was used to provide a preliminary QA check on the analytical results provided by the contract laboratory. The system detection limit should be comparable to the instrumental detection limit reported by the contract laboratory if there is no variability added as a result of sample collection, processing, and shipment.

Table 21 provides a summary of the field and laboratory blank data for 20 parameters from the ELS-I. Values for individual laboratories are listed in Appendix B. The required instrumental detection limits (IDLs) were achieved in the contract laboratories for all parameters except Fe and NO_3^-. However, for some of the parameters the system decision limit is considerably higher than the required IDL; this is possibly due to background sources of contamination.

The evaluation of blank data demonstrated that instrumental detection limit goals were generally achieved. However, to interpret the data, results from the field blanks must also be taken into consideration. Although extremely low detection limits can be achieved in the laboratory, they are of limited value in defining usable data when they are lower than the system detection limit (the background from sample collection and handling). The system decision limit may be considered as the limit for data interpretation with respect to population estimates. The use of the system decision limit in data interpretation is described in greater detail in Linthurst et al. (1986).

Duplicate Data

Data for estimating overall within-batch precision were obtained by using field duplicate samples. These were processed by the field laboratories and were analyzed with the routine samples and field blanks at the contract laboratories. The identity of the field duplicates was not disclosed to the contract laboratories. The field and contract laboratories also performed duplicate chemical analyses on one sample per batch as a QC check on analytical within-batch precision.

In total, 125 field duplicates were collected during the ELS-I. The estimates of overall within-batch precision obtained from field duplicate data include the effects of sample collection, processing, shipping, and analysis, but do not include the effects of among-batch variation that may have been caused by day-to-day differences such as different calibration curves.

Within-batch precision was calculated as the root mean square (RMS) of the percent relative standard deviation (%RSD) to estimate the 'average' %RSD over the range of values for routine-duplicate pairs. The estimated within-batch precision values are directly comparable to the intralaboratory precision goals which are also expressed as %RSD.

TABLE 21. INSTRUMENTAL DETECTION LIMITS, SYSTEM DETECTION LIMITS, AND SYSTEM DECISION LIMITS FOR 20 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

	Instrumental Detection Limit				
Parameter	Required[a]	Reported[b]	Estimated[c]	System Detection Limit[d]	System Decision Limit[e]
Al, mg L^{-1}					
total extractable	0.005	0.003	0.013	0.014	0.008
total	0.005	0.003	0.004	0.050	0.030
ANC, µeq L^{-1}	--f	--f	--f	11	6.9
Ca, mg L^{-1}	0.01	0.01	0.00	0.06	0.03
Cl^-, mg L^{-1}	0.01	0.01	0.05	0.13	0.08
Conductance, µS cm^{-1}	--g	0.0	1.6	1.4	1.3
DIC, mg L^{-1}					
air-equilibrated	0.05	0.03	0.14	0.20	0.28
initial	--h	--h	--h	0.38	0.42
DOC, mg L^{-1}	0.1	0.1	0.3	0.4	0.4
F^-, total dissolved, mg L^{-1}	0.005	0.002	0.008	0.008	0.005
Fe, mg L^{-1}	0.01	0.02	0.02	0.04	0.02
K, mg L^{-1}	0.01	0.00	0.00	0.03	0.02
Mg, mg L^{-1}	0.01	0.00	0.00	0.02	0.01
Mn, mg L^{-1}	0.01	0.01	0.01	0.02	0.01

(continued)

TABLE 21. (continued)

Parameter	Instrumental Detection Limit			System Detection Limit[d]	System Decision Limit[e]
	Required[a]	Reported[b]	Estimated[c]		
Na, mg L^{-1}	0.01	0.00	0.01	0.06	0.03
NH_4^+, mg L^{-1}	0.01	0.01	0.03	0.06	0.04
NO_3^-, mg L^{-1}					
all batches	0.005	0.006	0.037	0.760	0.389
aliquot 3	--	--	--	0.046	0.023
aliquot 5	--	--	--	1.782	0.919
P, total, mg L^{-1}	0.002	0.001	0.003	0.014	0.008
SiO_2, mg L^{-1}	0.05	0.02	0.06	0.21	0.11
SO_4^{2-}, mg L^{-1}	0.05	0.02	0.09	0.13	0.09

[a] The required instrumental detection limits (IDLs) are based on published literature (see Hillman et al. 1986).

[b] The arithmetic mean of all weekly reported IDLs for all ELS-I analytical laboratories. The weekly reported IDL = 3s, where s = the standard deviation of 10 nonconsecutive replicate laboratory calibration or reagent blank analyses (see Drousé et al. 1986).

[c] The estimated IDL = $[2(P_{95}-P_{50})]$, where P_{95} = 95th percentile, and P_5 = 50th percentile (median), of laboratory calibration blank samples (see Appendix A).

[d] The system detection limit = $[2(P_{95}-P_{50})]$, where P_{95} = 95th percentile, and P_{50} = 50th percentile (median), of field blank samples (see Appendix A).

[e] The system decision limit = (P_{95}), where P_{95} = 95th percentile of field blank samples (see Appendix A).

[f] The absolute value of each ANC measurement in laboratory calibration blanks was required to be ≤ 10 µeq L^{-1}.

[g] For conductance, the mean of six nonconsecutive laboratory calibration blank measurements was required to be less than 0.9 µS cm^{-1}.

[h] Measurements of laboratory calibration blanks not required.

A quantitation limit was calculated for each parameter to distinguish values which are expected a priori to have greater and more variable relative errors (i.e., values close to the detection limit) from values which are expected to have smaller and more consistant relative precision (values much greater than the detection limit). The quantitation limit should not be confused with instrumental detection limits, system detection limits, or system decision limits, all of which serve to constrain the actual size of the usable data set. All of the verified data, including values below the quantitation limits, were considered in the validation process; quantitation limits were calculated solely for the purpose of estimating the characteristic relative precision. A more detailed discussion of the statistical approach for evaluating within-batch and among-batch precision is provided in Appendix A.

Overall within-batch precision estimates for 23 parameters from the ELS-I are presented in Table 22. The three types of pH measurements were evaluated in terms of absolute rather than relative standard deviation. The estimated overall within-batch precision for pH in all four laboratories was within a range of 0.05 to 0.09 pH unit. No single laboratory had uniformly high or low precision; however, air-equilibrated pH data from Versar and initial ANC and BNC pH data from USGS had higher variability than the other measurements (see Appendix C).

The measured concentrations of some parameters (Ca, Mg, Na, SO_4^{2-}) were far above both the reported and the required instrumental detection limits. The results indicate that overall within-batch precision was better than the intralaboratory precision goal for each of these parameters. Most or all of these pairs had a mean concentration greater than the quantitation limit (see Table 22).

Other chemical parameters (Mn, Fe, total extractable Al, total Al, Cl^-, SiO_2, and total P) were characterized by low concentrations (at or below the quantitation limit) in many of the sample pairs. The relative precision of the data is characterized by a positive bias because the absolute variability of the measurement is greater near the instrumental detection limit (see Appendix A). Even if the absolute variability in the chemical analysis was uniform at all concentrations, an estimate of the true precision would be difficult to ascertain over the entire range of values when it is expressed as a percentage of the mean concentration.

The estimated precision for all duplicate data with concentrations greater than zero is also provided in Table 22. For these parameters, all pairs with concentrations above the quantitation limit had overall within-batch precision that was better than the overall intralaboratory precision goal, except for total extractable Al, total Al, Cl^-, DOC (for pairs with $\overline{X} > 5$ mg L^{-1}), Mn, NO_3^-, and SO_4^{-2}. The data user should again consider the estimated quantitation limit when interpreting the precision of data.

Duplicate analyses, designated as trailer duplicates, were also performed for all measurements made in the field laboratory. One trailer duplicate was analyzed per sample batch. This duplicate analysis was a QC step to assure consistent measurements within the field laboratory. A QC limit of ±0.1 pH unit was established for pH measurements, and a QC limit of ±10 percent was

TABLE 22. OVERALL WITHIN-BATCH PRECISION ESTIMATED FROM FIELD DUPLICATE DATA AND FIELD BLANK DATA FOR MEASUREMENTS OF 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

		Pairs with Mean >0			Pairs with Mean $>10s_B$[c]		
Parameter	RDL[a]	n[b]	Root Mean Square of %RSD[c]	Quantitation Limit $(10s_B)$[d]	n[b]	Root Mean Square of %RSD[c]	Overall Intra-laboratory Precision Goal (%RSD)[c]
Al, total extractable, mg L^{-1}							
all values	0.005	113	46	0.039	9	11	
$\bar{x} <= 0.010$		69	57		0	--	20
$\bar{x} > 0.010$		44	21		9	11	10
Al, total, mg L^{-1}							
all values	0.005	125	35	0.277	1	24	
$\bar{x} <= 0.010$		9	55		0	--	20
$\bar{x} > 0.010$		116	33		1	24	10
ANC, μeq L^{-1}	5	121	20	56.6	90	10	10
Ca, mg L^{-1}	0.01	125	2.3	0.14	125	2.3	5
Cl^-, mg L^{-1}	0.01	125	20	0.38	85	17	5
Conductance, μS cm^{-1}	--[e]	125	1.9	9.0	125	1.9	3
DIC, mg L^{-1}							
air-equilibrated	0.05	124	12	0.56	94	5.0	10
initial	0.05	125	6.9	1.09	85	3.7	10

(continued)

TABLE 22. (continued)

Parameter	RDL[a]	Pairs with Mean >0 n[b]	Pairs with Mean >0 Root Mean Square of %RSD[c]	Quantitation Limit $(10s_B)$[d]	Pairs with Mean $>10s_B$[d] n[b]	Pairs with Mean $>10s_B$[d] Root Mean Square of %RSD[c]	Overall Intra-laboratory Precision Goal (%RSD)[c]
DOC, mg L^{-1}							
all values	0.1	125	9.8	2.5	105	10	
$\overline{x}$ <= 5		66	6.7		46	5.6	10
$\overline{x}$ > 5		59	12		59	12	5
F^-, total dissolved, mg L^{-1}	0.005	125	8.1	0.034	62	8.9	5
Fe, mg L^{-1}	0.01	118	97	0.12	32	10	10
K, mg L^{-1}	0.01	125	4.7	0.37	82	3.7	10
Mg, mg L^{-1}	0.01	125	2.3	0.04	125	2.3	10
Mn, mg L^{-1}	0.01	82	57	0.093	6	11	10
Na, mg L^{-1}	0.01	125	4.2	0.20	121	4.3	5
NH_4^+, mg L^{-1}	0.01	113	34	0.56	0	--	10
NO_3^-, mg L^{-1}							
all batches	0.005	113	443	0.894	5	60	10
aliquot 3		45	213	0.163	9	45	
aliquot 5		68	544	1.143	0	--	

(continued)

TABLE 22. (continued)

Parameter	RDL[a]	Pairs with Mean >0 n[b]	Pairs with Mean >0 Root Mean Square of %RSD[c]	Quantitation Limit $(10s_B)$[d]	Pairs with Mean $>10s_B$[d] n[b]	Pairs with Mean $>10s_B$[d] Root Mean Square of %RSD[c]	Overall Intra-laboratory Precision Goal (%RSD)[c]
pH							
air-equilibrated	--[f]	125	0.09[g]	--[f]	--[f]	--[f]	0.05[h]
initial ANC	--[f]	125	0.05[g]	--[f]	--[f]	--[f]	0.05[h]
initial BNC	--[f]	125	0.07[g]	--[f]	--[f]	--[f]	0.05[h]
P, total, mg L^{-1}							
all values	0.002	122	37	0.037	4	9.7	
$\overline{x} <= 0.010$		57	44		0	--	20
$\overline{x} > 0.010$		65	30		4	9.7	10
SiO_2, mg L^{-1}	0.05	120	44	2.34	50	2.7	5
SO_4^{2-}, mg L^{-1}	0.05	125	6.6	1.68	115	6.5	5

[a] RDL = required detection limit (in applicable units).

[b] n = number of routine/field duplicate pairs.

[c] %RSD = percent relative standard deviation.

[d] s_B = standard deviation of field blank measurements (see Appendix A) with n = 245 except for total Al, n = 244; NH_4^+, n = 243; NO_3^-, aliquot 3, n = 99; and NO_3^-, aliquot 5, n = 145.

[e] For conductance, the mean of six nonconsecutive replicate calibration blank measurements was required to be less than 0.9 µS cm^{-1}.

[f] Not applicable.

[g] Root mean square of absolute standard deviation (pH unit).

[h] Absolute precision goal (pH unit).

established for DIC, true color, and DIC measurements. If the QC limits were exceeded, the laboratory was required to analyze a second duplicate. If the limits were still exceeded after reanalysis, the laboratory supervisor made additional efforts to identify and correct the problem until it was resolved.

Precision estimates from field duplicate and trailer duplicate data are presented in Table 23. For trailer duplicates, the observed analytical within-batch precision for each parameter was within the analytical intralaboratory precision goal established for the ELS-I. The overall within-batch precision for field duplicates was within the overall intralaboratory precision goal for pH, but was not for DIC, true color, or turbidity. Gross observation of the data revealed that there was little bias apparent among field stations for these analyses. Bias is discussed in greater detail in Appendix A.

The contract laboratories were required to analyze one sample per batch in duplicate. For each parameter, the analytical within-batch precision was required to be within the analytical intralaboratory precision goal. Analytical within-batch precision estimates from contract analytical laboratory duplicate pH data are presented in Table 24. The results for pH indicate that precision was within a range of ±0.04 to 0.08 pH unit. These data may have been biased because the laboratory analysts knew which samples were duplicates, and they knew that the required precision goal must be achieved. However, the results are an indication of the precision that was achieved within each laboratory with the method QC requirements.

TABLE 23. OVERALL AND ANALYTICAL WITHIN-BATCH PRECISION ESTIMATED FROM FIELD DUPLICATE AND TRAILER DUPLICATE DATA FOR MEASUREMENTS OF FOUR PARAMETERS, EASTERN LAKE SURVEY - PHASE I

		Overall Within-Batch Precision (Field Duplicates)		Analytical Within-Batch Precision (Trailer Duplicates)	
Parameter	Overall and Analytical Intralaboratory Precision Goal (%RSD)[a]	n[b]	Root Mean Square of %RSD[a]	n[b]	Root Mean Square of %RSD[a]
pH	0.1[c]	124	0.04[d]	93	0.01[d]
DIC, mg L^{-1}	10	123	16	116	4.6
True color, PCU	10	125	22	118	1.5
Turbidity, NTU	10	125	19	117	8.4

[a] RSD = relative standard deviation.

[b] n = number of duplicate pairs.

[c] Absolute standard deviation (pH unit).

[d] Root mean square of absolute standard deviation (pH unit).

Precision estimates for the other 20 parameters from contract laboratory duplicate data are also shown in Table 24. The estimated analytical within-batch precision for pairs with mean >10s_B was better than the analytical intralaboratory precision goal for each of the parameters except total extractable Al > 0.010 mg L^{-1}, Cl^-, Mn, SO_4^{2-}, and conductance.

In general, the overall and analytical intralaboratory precision goals were achieved between values for routine-field duplicate pairs as well as between contract laboratory duplicate pairs. The exceptions to these results are discussed in Section 5. Thus, the estimated within-batch precision was considered to be adequate to meet the DQOs established at the beginning of the ELS-I (see Table 1).

Audit Sample Data

Audit sample data can be used to obtain estimates of among-batch precision and interlaboratory bias (see Table 3). Six types of audit samples (2 field naturals, 2 field synthetics, and 2 laboratory synthetics) were analyzed for 23 parameters during the ELS-I. Field naturals and field synthetics were handled in the same manner as routine, field blank, and field duplicate samples (see Section 2) to estimate the overall among-batch precision including the effects of sample processing. Laboratory synthetics were prepared as processed aliquots by a support laboratory; these were relabeled at the field laboratory and were incorporated with the sample batch to estimate analytical among-batch precision.

The natural audit samples were also used to estimate relative interlaboratory bias by comparing measured values from the contract laboratories with each other and with referee laboratory measurements. The synthetic audits were used to provide information on absolute interlaboratory bias; this required that they be prepared from solutions of known composition. Examination of both the theoretical values and the measured values for synthetic audit samples indicated that the actual sample composition may have differed on different days and that measurement imprecision and interlaboratory bias were small by comparison (see Appendix A).

One type of field natural sample (FN2, from Big Moose Lake in the Adirondack Mountains, New York) was representative of lakes which are sensitive to acidic deposition; the other type (FN3, from Lake Superior near Duluth, Minnesota) represented systems with high ANC. In total, 41 FN2 samples and 7 FN3 samples were used during the survey. Two concentrations of synthetic audit samples were also prepared. These synthetic audits included 36 field highs, 21 laboratory highs, 42 field lows, and 43 laboratory lows.

Table 25 summarizes the mean sample composition and the overall among-batch precision for 23 parameters estimated from FN2 and FN3 data. Mean values were less than the quantitation limits for 7 parameters measured in the FN2 samples and for 7 parameters measured in the FN3 samples. For ANC, air-equilibrated DIC, and initial DIC, the estimated precision was better, i.e., the %RSD was lower, for the FN3 samples (which had means greater than the quantitation limits) than for the FN2 samples (which had means less than the quantitation limits). This is consistent with our expectations. The precision of the total extractable Al, total Al, and DOC measurements was slightly better

TABLE 24. ANALYTICAL WITHIN-BATCH PRECISION ESTIMATED FROM CONTRACT LABORATORY DUPLICATE DATA AND CALIBRATION BLANK DATA FOR MEASUREMENTS OF 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

Parameter	RDL[a]	Pairs with Mean >0		Quantitation Limit $(10s_B)$[d]	Pairs with Mean $>10s_B$[d]		Analytical Intralaboratory Precision Goal (%RSD)[c]
		n[b]	Root Mean Square of %RSD[c]		n[b]	Root Mean Square of %RSD[c]	
Al, total extractable, mg L^{-1}							
all values	0.005	123	13	0.038	46	18	20
$\bar{x}$ <= 0.010		22	14		0	--	10
$\bar{x}$ > 0.010		101	12		46	18	
Al, total, mg L^{-1}							
all values	0.005	126	19	0.012	9	5.4	20
$\bar{x}$ <= 0.010		8	57		0	--	10
$\bar{x}$ > 0.010		118	12		9	5.4	
ANC, µeq L^{-1}	5	116	30	56.6[f]	86	2.1	10
Ca, mg L^{-1}	0.01	123	0.88	0.04	123	0.88	5
Cl^-, mg L^{-1}	0.01	127	23	0.11	124	7.1	5
Conductance, µS cm^{-1}	--e	125	11	5.4	123	10	1
DIC, mg L^{-1}							
air-equilibrated	0.05	126	7.1	0.60	94	2.2	10
initial	0.05	127	3.7	0.54	113	3.5	10

(continued)

TABLE 24. (continued)

		Pairs with Mean >0			Pairs with Mean $>10s_B$[d]		
Parameter	RDL[a]	n[b]	Root Mean Square of %RSD[c]	Quantitation Limit $(10s_B)$[d]	n[b]	Root Mean Square of %RSD[c]	Analytical Intra-laboratory Precision Goal (%RSD)[c]
DOC, mg L^{-1}							
all values	0.1	126	6.8	1.0	114	2.4	
$\bar{x} <= 5$		85	8.1		73	2.5	10
$\bar{x} > 5$		41	2.4		41	2.4	5
F^-, total dissolved, mg L^{-1}	0.005	127	2.5	0.015	123	2.5	5
Fe, mg L^{-1}	0.01	120	14	0.05	101	4.3	10
K, mg L^{-1}	0.01	125	18	0.04	121	1.5	5
Mg, mg L^{-1}	0.01	121	0.64	0.01	121	0.64	5
Mn, mg L^{-1}	0.01	102	21	0.030	73	17	10
Na, mg L^{-1}	0.01	123	13	0.10	121	0.96	5
NH_4^+, mg L^{-1}	0.01	121	7.1	0.15	54	2.3	5
NO_3^-, mg L^{-1}							
all batches	0.005	122	13	0.157	86	3.6	10
aliquot 3		51	20	0.110	39	3.7	
aliquot 5		71	3.9	0.185	46	3.3	

TABLE 24. (continued)

Parameter	RDL[a]	Pairs with Mean >0 n[b]	Pairs with Mean >0 Root Mean Square of %RSD[c]	Quantitation Limit ($10s_B$)[d]	Pairs with Mean >$10s_B$[d] n[b]	Pairs with Mean >$10s_B$[d] Root Mean Square of %RSD[c]	Analytical Intralaboratory Precision Goal (%RSD)[c]
pH							
air-equilibrated	--g	127	0.08h	--g	--g	--g	0.05i
initial ANC	--g	127	0.04h	--g	--g	--g	0.05i
initial BNC	--g	127	0.07h	--g	--g	--g	0.05i
P, total, mg L^{-1}							
all values	0.002	125	13	0.008	104	9.9	--
$\overline{x}$ <= 0.010		30	20		9	8.6	20
$\overline{x}$ > 0.010		95	10		95	10	10
SiO_2, mg L^{-1}	0.05	127	2.5	2.37	64	2.2	5
SO_4^{2-},mg L^{-1}	0.05	127	11	0.18	124	11	5

[a] RDL = required detection limit (in applicable units).

[b] n = number of contract laboratory duplicate pairs.

[c] %RSD = percent relative standard deviation.

[d] s_B = standard deviation of measurements of contract laboratory calibration blanks with n = 127 except for DIC, n = 125; Mn, n = 126; NO_3^-, aliquot 3, n = 53; and NO_3^-, aliquot 5, n = 72.

[e] For conductance, the mean of six nonconsecutive replicate calibration blank measurements was required to be less than 0.9 µS cm^{-1}.

[f] Quantitation limit calculated using field blank data (see text).

[g] Not applicable.

[h] Root mean square of absolute standard deviation (pH unit).

[i] Absolute standard deviation (pH unit).

TABLE 25. OVERALL AMONG-BATCH PRECISION ESTIMATED FROM FIELD NATURAL, LOT 2 (FN2, BIG MOOSE LAKE) AND FIELD NATURAL, LOT 3 (FN3, LAKE SUPERIOR) AUDIT SAMPLE DATA FOR MEASUREMENTS OF 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

	FN2 (n = 41)		FN3 (n = 7)		Quantitation Limit
Parameter	Mean	%RSD[a]	Mean	%RSD[a]	($10s_B$)[b]
Al, mg L^{-1}					
total extractable	0.182	34	0.002[e]	87	0.039
total	0.305	28	0.021[e]	123	0.277
ANC, µeq L^{-1}	2.4[e]	258	848.2	2.3	56.6
Ca, mg L^{-1}	1.91	9.2	13.28	5.5	0.14
Cl^-, mg L^{-1}	0.61	51	1.39	2.0	0.38
Conductance, µS cm^{-1}	26.7	3.6	96.4	1.7	9.0
DIC, mg L^{-1}					
air-equilibrated	0.19[e]	60	9.68	3.8	0.56
initial	0.42[e]	27	9.93	4.2	1.09
DOC, mg L^{-1}	3.3	9.3	1.4[e]	9.7	2.5
F^-, total dissolved, mg L^{-1}	0.077	4.0	0.035	5.2	0.034
Fe, mg L^{-1}	0.02[e]	66	0.00[e]	137	0.12
K, mg L^{-1}	0.49	4.3	0.49	12	0.37
Mg, mg L^{-1}	0.35	2.7	2.79	3.6	0.04
Mn, mg L^{-1}	0.07[e]	26	0.00[e]	362	0.093
Na, mg L^{-1}	0.67	5.1	1.30	6.4	0.20
NH_4^+, mg L^{-1}	0.06[e]	54	0.01[e]	130	0.56
NO_3^-, mg L^{-1}					
all batches	1.425	5.5	1.401	5.8	0.894
aliquot 3[c]	1.473	3.0	1.422	3.6	0.163
aliquot 5[d]	1.403	5.8	1.385	8.5	1.143

(continued)

TABLE 25. (continued)

Parameter	FN2 (n = 41)		FN3 (n = 7)		Quantitation Limit $(10s_B)$[b]
	Mean	%RSD[a]	Mean	%RSD[a]	
pH					
air-equilibrated	5.18	0.27[f]	8.23	0.08[f]	--[g]
initial ANC	5.07	0.04[f]	7.76	0.12[f]	--[g]
initial BNC	5.08	0.05[f]	7.79	0.12[f]	--[g]
P, total, mg L^{-1}	0.002[e]	144	0.001[e]	143	0.037
SiO_2, mg L^{-1}	4.33	8.1	2.72	6.0	2.34
SO_4^{2-}, mg L^{-1}	6.95	7.3	3.26	3.3	1.68

[a] Percent relative standard deviation.
[b] s_B = standard deviation of measurements of field blank samples (see Appendix A).
[c] Aliquot 3 samples after filtration protocol change (FN2, n = 13; FN3, n = 4).
[d] Aliquot 5 samples (FN2, n = 28; FN3, n = 3).
[e] Mean less than quantitation limit.
[f] Absolute standard deviation.
[g] Quantitation limits not applicable for pH measurements.

with the FN2 samples than with the FN3 samples; for those parameters the mean FN3 values were less than the quantitation limits. A test of significance of the differences between the precision of these measurements was not performed because of the small number of FN3 samples that was used.

The mean values in the FN2 samples and in the FN3 samples were less than the quantitation limits for Fe, Mn, NH_4^+, and total P, and the means in both sample types were greater than the quantitation limits for 10 parameters. Quantitation limits were not applicable for the three pH measurements. For the field natural audit samples with means greater than the quantitation limits, the overall interlaboratory precision goal (estimated as twice the overall intralaboratory precision goal, see Table 22) was achieved for all parameters except total extractable Al, total Al, and Cl^- in the FN2 samples and for all parameters in the FN3 samples.

Tables 26 and 27 summarize the mean values for sample composition and the overall and analytical among-batch precision estimated from measurements of synthetic audit samples. For the field high synthetics, the mean value for total Al was less than the quantitation limit; all other parameters (except pH) had means above the quantitation limits. The overall interlaboratory precision goal was not met for total Al, as was expected, and was also not met for Cl^-, air-equilibrated and initial DIC, DOC, Mn, NH_4^+, NO_3^-, and SiO_2. Means for laboratory high synthetics were greater than quantitation limits for all parameters (not applicable for pH). Analytical interlaboratory precision goals were

TABLE 26. MEAN MEASURED VALUES, OVERALL AND ANALYTICAL AMONG-BATCH PRECISION ESTIMATES, AND THEORETICAL CONCENTRATIONS OF HIGH SYNTHETIC AUDIT SAMPLES, EASTERN LAKE SURVEY - PHASE I

	Overall Among-Batch Precision			Analytical Among-Batch Precision			
	Field Highs		Quantitation Limit (10s_B)[b]	Laboratory Highs		Quantitation Limit (10s_B)[b]	
Parameter	$\overline{X}$ (n=36)	%RSD[a]		$\overline{X}$ (n=31)	%RSD[a]		Theoretical Value
Al, mg L^{-1}							
total extractable[c]	--	--	0.039	0.161	19	0.038	--[h]
total	0.199[d]	30	0.277	0.194	34	0.012	0.19
ANC, μeq L^{-1}	476.7	17	56.6	485.9	20	56.6[g]	--[h]
Ca, mg L^{-1}			0.14			0.04	
Lot 4 (n=20,14)	1.66	6.6		1.55	12		1.54
Lot 5 and 6 (n=16, 7)	1.95	8.2		1.96	5.1		2.39
Cl^-, mg L^{-1}			0.38			0.11	
Lot 4 (n=15, 14)	3.66	40		3.39	7.1		2.72
Lot 5 and 6 (n=16,7)	4.00	18		5.81	92		4.22
Conductance, μS cm^{-1}	104.5	4.0	9.0	104.3	3.9	5.4	--[h]
DIC, mg L^{-1}							
air-equilibrated	4.72	27	0.56	4.79	27	0.60	--[h]
initial	5.94	33	1.09	5.94	32	0.54	3.10
DOC, mg L^{-1}	10.0	20	2.5	10.3	16	1.0	10.0
F^-, total dissolved, mg L^{-1}	0.445	9.4	0.034	0.435	2.8	0.015	0.452

(continued)

TABLE 26. (continued)

	Overall Among-Batch Precision			Analytical Among-Batch Precision			
	Field Highs			Laboratory Highs			
Parameter	$\overline{X}$ (n=36)	%RSD[a]	Quantitation Limit $(10s_B)$[b]	$\overline{X}$ (n=31)	%RSD[a]	Quantitation Limit $(10s_B)$[b]	Theoretical Value
Fe, mg L^{-1}	--	--	0.12	0.18	11	0.05	0.15
K, mg L^{-1}	3.03	6.3	0.37	3.02	5.0	0.04	2.97
Mg, mg L^{-1}	2.37	3.8	0.04	2.36	3.4	0.01	2.43
Mn, mg L^{-1}	1.19	13	0.093	1.39	2.9	0.030	1.50
Na, mg L^{-1}	11.84	8.7	0.20	11.87	8.8	0.10	12.41
NH_4^+, mg L^{-1}	1.26	13	0.56	1.34	13	0.15	1.25
NO_3^-, mg L^{-1} (all batches)	1.816	37	0.894	1.431	47	0.157	1.707
pH							
air-equilibrated	7.72	0.54[e]	--[g]	7.87	0.15[e]	--[g]	--[h]
initial ANC	7.08	0.25[e]	--[g]	7.05	0.26[e]	--[g]	--[h]
initial BNC	7.12	0.27[e]	--[g]	7.11	0.25[e]	--[g]	--[h]
P, total, mg L^{-1}	0.057	23	0.037	0.061	16	0.008	0.075
SiO_2, mg L^{-1}	9.23	14	2.34	9.42	15	2.37	10.70
SO_4^{2-}, mg L^{-1}	14.39	5.6	1.68	14.47	4.8	0.18	14.09

[a] Percent relative standard deviation.

[b] s_B=standard deviation of measurements of field blank or laboratory blank samples (see Appendix A).

[c] Laboratory synthetic audit samples only.

[d] Mean less than quantitation limit.

[e] Absolute standard deviation (pH unit).

[f] Quantitation limits not applicable for pH measurements.

[g] Quantitation limit calculated by using field blank data.

[h] Theoretical concentration not available.

TABLE 27. MEAN MEASURED VALUES, OVERALL AND ANALYTICAL AMONG-BATCH PRECISION ESTIMATES, AND THEORETICAL CONCENTRATIONS OF LOW SYNTHETIC AUDIT SAMPLES, EASTERN LAKE SURVEY - PHASE I

	Overall Among-Batch Precision			Analytical Among-Batch Precision			
	Field Lows		Quantitation Limit $(10s_B)$[b]	Laboratory Lows		Quantitation Limit $(10s_B)$[b]	
Parameter	$\overline{X}$ (n=43)	%RSD[a]		$\overline{X}$ (n=43)	%RSD[a]		Theoretical Value
Al, mg L^{-1}							
total extractable[c]	--	--	0.039	0.018[d]	33	0.038	--[f]
total	0.023[d]	22	0.277	0.031	90	0.012	0.02
ANC, µeq L^{-1}	112	7.4	56.6	110	9.4	56.69	--[f]
Ca, mg L^{-1}			0.14			0.04	
Lot 4 (n=23, 23)	0.14[d]	19		0.14	11		0.13
Lot 5 and 6 (n=20, 20)	0.17	7.1		0.16	8.7		0.19
Cl^-, mg L^{-1}			0.38			0.11	
Lot 4 (n=23, 23)	0.33[d]	71		0.30	14		0.22
Lot 5 and 6 (n=20, 20)	0.37[d]	22		0.35	31		0.34
Conductance, µS cm^{-1}	19.0	6.8	9.0	18.7	6.4	5.4	--[f]
DIC, mg L^{-1}							
air-equilibrated	1.35	8.9	0.56	1.35	11	0.60	--[f]
initial	1.65	13	1.09	1.65	15	0.54	0.96
DOC, mg L^{-1}	1.0[d]	48	2.5	1.2	61	1.0	1.0
F^-, total dissolved, mg L^{-1}	0.042	21	0.034	0.040	5.0	0.015	0.042

(continued)

TABLE 27. (continued)

	Overall Among-Batch Precision			Analytical Among-Batch Precision			
	Field Lows			Laboratory Lows			
Parameter	$\overline{X}$ (n=43)	%RSD[a]	Quantitation Limit ($10s_B$)[b]	$\overline{X}$ (n=43)	%RSD[a]	Quantitation Limit ($10s_B$)[b]	Theoretical Value
Fe, mg L^{-1}[c]	--	--	0.12	0.07	23	0.05	0.06
K, mg L^{-1}	0.23[d]	19	0.37	0.23	10	0.04	0.20
Mg, mg L^{-1}	0.42	7.3	0.04	0.43	4.5	0.01	0.45
Mn, mg L^{-1}	0.091[d]	10	0.093	0.092	16	0.030	0.10
Na, mg L^{-1}	2.71	5.2	0.20	2.69	9.3	0.10	2.79
NH_4^+, mg L^{-1}	0.16[d]	27	0.56	0.19	22	0.15	0.17
NO_3^-, mg L^{-1}	0.547[d]	66	0.894	0.471	37	0.157	0.466
pH							
air-equilibrated	7.34	0.14[e]	--[f]	7.29	0.13[e]	--[f]	--[f]
initial ANC	6.87	0.11[e]	--[f]	6.86	0.12[e]	--[f]	--[f]
initial BNC	6.96	0.19[e]	--[f]	6.93	0.15[e]	--[f]	--[f]
P, total, mg L^{-1}	0.021[d]	29	0.037	0.022	41	0.008	0.027
SiO_2, mg L^{-1}	1.00[d]	31	2.34	1.02[d]	20	2.37	1.07
SO_4^{2-}, mg L^{-1}	2.27	10	1.68	2.28	4.4	0.18	2.28

[a] Percent relative standard deviation.

[b] s_B=standard deviation of measurements of field blank or laboratory blank samples (see Appendix A).

[c] Laboratory synthetic audit samples only.

[d] Mean equal to or less than quantitation limit.

[e] Absolute standard deviation (pH unit).

[f] Not applicable.

[g] Quantitation limit calculated by using field blank data.

met for all parameters except total Al, Ca (Lot 4), Cl^- (Lots 5 and 6), conductance, air-equilibrated and initial DIC, Mn, NH_4^+, NO_3^-, and SiO_2.

The mean values in the field low synthetics were less than the quantitation limits for total Al, Cl^-, DOC, K, Mn, NH_4^+, NO_3^-, total P, and SiO_2 (not applicable for pH). The mean of Ca (Lot 4) values in field lows was equal to the quantitation limit. Of these 13 parameters, the overall interlaboratory precision goals were attained only for K and Mn. The mean values for the other 10 parameters measured in the field low synthetics were greater than the quantitation limits. Of these 10 parameters, the overall interlaboratory precision goals were met by all parameters except conductance and total dissolved F^-. The means for the laboratory low synthetics were greater than the quantitation limits for all parameters except total extractable Al and SiO_2 (not applicable for pH). The analytical interlaboratory precision goals were met for ANC, Ca (Lots 5 and 6), air-equilibrated and initial DIC, total dissolved F^-, K, Mn, Na, NH_4^+, and SO_4^{-2}; they were not met by the other 13 parameters.

It is evident from the results for synthetic audit samples that the levels of among-batch precision expected for these measurements were generally attained for parameters with high sample values, and they were generally not attained for parameters with low sample values. The imprecision for parameters with high sample values was presumably related to mixing error or sample instability or both; these discrepancies are discussed in greater detail in Appendix A.

The results for field and laboratory audit samples also show that quantitation limits were a useful means of classifying the data, which was necessary to objectively evaluate among-batch precision estimates for the 23 parameters. It was possible to determine whether the observed precision estimates for each parameter were reasonable in relation to the DQOs established for the survey. High precision was not expected for measurements close to the detection limits, and it was not achieved for any parameters with means less than quantitation limits except DOC. Conversely, high precision was expected and was generally achieved for measurements with higher mean values (i.e., for all but 3 parameters with FN2 samples and for all parameters with FN3 samples). The estimated overall and analytical within-batch precision of DOC measurements showed a pattern which was opposite to that shown by all other parameters; measurements at higher concentrations exhibited greater variability than measurements at lower concentrations. This pattern is thought to be related to instrument performance characteristics.

Natural and synthetic audit samples were also used to judge the performance of contract analytical laboratories on a batch basis (Drousé et al., 1986). Table 28 provides examples of the 95 percent confidence intervals (performance windows) that were used for data evaluation. Actual laboratory performance was judged according to 95 percent confidence intervals for each lot of each type of audit sample. Any audit sample outside the interval was flagged for further verification. These flags were used to concentrate verification efforts on potential analytical problems. Field synthetic audit samples were assumed to contain precipitated Fe and Al which were removed by filtering at the field laboratory; those samples were not included in the statistical evaluation.

TABLE 28. CONTRACT ANALYTICAL LABORATORY PERFORMANCE WINDOWS FOR AUDIT SAMPLE MEASUREMENTS, EASTERN LAKE SURVEY - PHASE I

Parameter	FN2^a		FN3^b		Field and Laboratory High Synthetics		Field and Laboratory Low Synthetics	
	High	Low	High	Low	High	Low	High	Low
Al, mg L^{-1}								
total extractable^c	0.308	0.056	0.007	-0.003	0.22	0.10	0.03	0.01
total	0.443	0.195	0.023	-0.006	0.27	0.14	0.04	0.01
ANC, µeq L^{-1}	14.8	-10.1	868.0	815.1	654.4	305.9	128.3	94.4
Ca, mg L^{-1}	2.03	1.75	13.95	12.12	2.21	1.30	0.19	0.11
Cl$^-$, mg L^{-1}	0.61	0.45	1.46	1.32	4.35	2.67	0.38	0.23
Conductance, µS cm^{-1}	28.0	25.2	100.5	92.3	112.9	96.1	21.1	16.5
DIC, mg L^{-1}								
air-equilibrated	0.21	0.10	10.61	8.76	7.29	2.14	1.61	1.11
initial	0.61	0.21	10.99	8.88	9.88	1.99	2.07	1.24
DOC, mg L^{-1}	3.5	2.9	1.7	1.0	14.5	6.1	1.9	0.1
F$^-$, total dissolved, mg L^{-1}	0.083	0.071	0.039	0.030	0.471	0.404	0.045	0.036
Fe, mg L^{-1}^{c}	0.04	-0.00	0.01	-0.01	0.21	0.15	0.09	0.05
K, mg L^{-1}	0.53	0.45	0.57	0.46	3.30	2.83	0.27	0.18
Mg, mg L^{-1}	0.36	0.33	3.05	2.54	2.54	2.20	4.58	0.39

(continued)

TABLE 28. (continued)

Parameter	FN2[a]		FN3[b]		Field and Laboratory High Synthetics		Field and Laboratory Low Synthetics	
	High	Low	High	Low	High	Low	High	Low
Mn, mg L^{-1}	0.08	0.06	0.00	-0.01	1.58	0.94	0.10	0.08
Na, mg L^{-1}	0.74	0.60	1.51	1.09	13.87	9.76	2.98	2.45
NH_4^+, mg L^{-1}	0.12	0.00	0.03	-0.02	1.58	0.97	0.25	0.10
NO_3^-, mg L^{-1}	1.557	1.316	1.607	1.205	3.090	0.264	0.927	0.037
pH								
air-equilibrated	5.20	5.07	8.28	8.19	8.14	7.58	7.59	7.04
initial ANC	5.15	4.98	8.07	7.44	7.57	6.56	7.09	6.63
initial BNC	5.18	4.98	8.08	7.49	7.64	6.58	7.21	6.65
P, total, mg L^{-1}	0.006	-0.003	0.007	-0.004	0.078	0.038	0.031	0.010
SiO_2, mg L^{-1}	5.05	3.62	3.14	2.31	11.90	6.74	1.43	0.57
SO_4^{2-}, mg L^{-1}	7.52	6.20	3.54	2.99	15.67	13.05	2.47	2.09

[a] FN2 = Field natural, lot 2 (Big Moose Lake).
[b] FN3 = Field natural, lot 3 (Lake Superior).
[c] Laboratory synthetic audit samples only.

Summary and Review of the External Data Evaluation

An additional statistical evaluation of the ELS-I data was provided by Permutt and Pollack (1986), and it is included in this report as Appendix A. A summary of their evaluation is provided below. The estimated system decision limits, system detection limits, quantitation limits, relative precision, and accuracy (absolute and relative interlaboratory bias and trend) were based on the field blank, field and laboratory duplicate, and natural and synthetic audit sample data. The assumptions and rationales used for the statistical analyses are presented, and the advantages and disadvantages of each type of analysis are discussed. The effects of removing QA data outliers are also discussed. The significance of these estimates to the overall quality of the ELS-I data is presented in a summary section with recommendations for improving specific aspects of the QA program design.

The evaluations of detectability in the Permutt and Pollack report were based on the distribution and the variability of the field blank measurements. For these evaluations it was assumed that the amount of background in the measurement system is independent of the analyte concentration in the sample. The system decision limit was defined, following Hubaux and Vos (1970), as "the lowest signal that can be distinguished from background"; i.e., a measurement so high that it rarely occurs in blank sample. The system decision limit was calculated by choosing an error ratio (α) and then estimating the upper α quantile of the background distribution. For the ELS-I, the system decision limit was calculated as the 95th percentile (P_{95}) of the field blank measurements. Measurements higher than P_{95} occur only 5 percent of the time for blank samples, so such a measurement is a significant indication at the 95 percent confidence level that the sample in question is not a blank.

The system detection limit was defined for the purpose of this study as the true concentration at which the probability is β that a measured concentration is above the decision limit. The system detection limit thus depends on the system decision limit and also, therefore, on the distribution of blank sample measurements. The relationships between the system detection and decision limits and the distribution of blank sample measurements is illustrated in Figure 2-2 of Permutt and Pollack (1986).

The estimate of the quantitation limit is based on the assumption that measurement variability is uniform over the range of sample concentrations. If the absolute standard deviation for the samples is the same as that for blanks then the relative standard deviation (RSD) would be more than 10 percent for any true concentration up to 10 s, and it would be less than 10 percent for any concentration above 10 s. At concentrations below the quantitation limit, high relative precision is not expected solely because of the arithmetic treatment of the data. The use of 10 s as the 'limit of quantitation' was reported by Long and Winefordner (1983).

The precision of the ELS-I duplicate sample data is expressed as the root mean square (RMS) of the percent RSD by Permutt and Pollack using this approach. Because the RMS is an estimate of the mean percent RSD over a range of sample concentrations, that estimate is dependent on the distribution of concentrations in the population. Two sets of precision values are presented for each parameter measured in the analytical laboratories for the ELS-I. The precision is calculated for the pairs with mean concentrations equal to or greater than the quantitation limit, and it is also calculated for the pairs which have mean concentrations greater than zero. The RMS of the percent RSD for field duplicate pairs is an estimate of the measurement variability on a given day that can be associated with sample collection, handling, and analysis; it is termed the overall within-batch precision. For the analytical laboratory duplicate pairs (split samples), the RMS of the percent RSD provides an estimate of the measurement variability on a given day that is associated only with sample analysis; it is termed the analytical within-batch precision. The difference between the values for overall and analytical within-batch precision can be used to estimate the amount of measurement variability on a given day that is associated with sample collection and handling.

Permutt and Pollack (1986) also evaluated the measurements of field natural audit samples and of field and laboratory synthetic audit samples from the ELS-I. The natural audit sample measurements provide information about relative interlaboratory bias (systematic differences between two laboratories), because they are repeated measurements by different laboratories from a single population of samples. The absolute bias (accuracy) in the measurements cannot be determined by using natural audit samples because the true composition of natural audits is not known. However, the natural audit sample data can also be used to estimate the precision (random variability) and the trend (systematic variability over time) in the measurements.

An analysis of covariance was used to quantify the bias and the trend in FN-2 (Big Moose Lake audit sample) measurements. The bias was quantified as the vertical distance between the least-square lines for the laboratories, and the trend was quantified by the common slope (the slope of the measurements corrected for bias). The absolute precision of the corrected measurements was estimated as the standard deviation of the measured values around their respective least-square lines.

The estimated relative interlaboratory bias in the FN-2 measurements is presented as a function of the mean for all laboratories and for each laboratory relative to each other laboratory. The standard error of each estimate provides a measure of its statistical uncertainty. For all of the parameters measured in the analytical laboratories, there is little difference between the estimated precision of the corrected and the uncorrected measurements; i.e., the biases and trends are small compared to the imprecision even though the systematic differences are sometimes large enough to be statistically significant. Furthermore, in many cases the bias or the trend is small compared to the standard error of the estimate (i.e., the evidence that there is any bias or trend at all is not statistically significant).

The FN-3 (Lake Superior audit sample) measurements were not corrected for bias or trend because the sample size (n=7) was insufficient for an analysis of covariance. Precision estimates are presented for the uncorrected measurements.

The measurements of field synthetic and laboratory synthetic audit samples were intended for use in three aspects of data quality assessment. These include estimation of precision and of relative interlaboratory bias; estimation of accuracy (absolute bias); and evaluation of measurement variability associated with sample handling.

Evidence is presented to demonstrate that the synthetic audit sample data are not repeated measurements from the same population. As an example, the NH_4^+ values are shown to be in close agreement within and among laboratories on a given day but to be very different on different days. An analysis of variance was used to quantify this comparison. It was concluded that the amount of data available for the synthetic audit samples is insufficient for estimating the measurement errors reliably.

The theoretical concentrations of 16 parameters in the synthetic audit samples were compared with the measured values. It was concluded on the basis of the close agreement between the values for most of the parameters that the measurement system was operating effectively. The measured concentrations of Fe and Mn in the field synthetic audit samples were considerably lower than the theoretical values, but in the laboratory synthetic audit samples the theoretical concentrations were close to the measured concentrations. A similar difference was observed between the field and the laboratory synthetic audit samples for measured concentrations of total extractable Al. This evidence suggests that Fe, Mn, and total extractable Al were removed from the field synthetic audits during processing in the field (see Methods Evaluation, above). It is also suggested that the discrepancies in the values for initial DIC, alkalinity (ANC), acidity (BNC), pH, Na and SiO_2 may have been caused by a change in the concentration of sodium silicate in the stock solution partially through the survey.

Overall, the field synthetic audit sample data were found to be no more variable than the laboratory synthetic data. Furthermore, the variability introduced at the audit sample preparation laboratory greatly exceeded the variability from sample processing and from sample analysis. It was concluded that the sources of measurement error could not be distinguished from each other on the basis of the synthetic audit sample data.

The relationships between the precision estimates are illustrated in Permutt and Pollack's report by using the Ca data from field and laboratory duplicate measurements and from field natural, field synthetic, and laboratory synthetic, audit sample measurements. The usefulness of the different types of audit samples is discussed in relation to their composition and to the numbers of samples analyzed.

The authors concluded that, overall, the imprecision of a perfectly calibrated instrument under constant conditions is small in comparison to the bias and trend introduced by procedural variations and by changes in the sample composition over time. The precision estimates from field natural audit samples were considered to be the best indicators of measurement uncertainty in the routine samples. The use of laboratory synthetic audit samples was recommended for estimating accuracy and relative interlaboratory bias. Daily lots of audit samples should be prepared and divided into aliquots, and the aliquots should be assigned to different analytical laboratories at random. Interlaboratory comparisons should be made using data from the same audit sample lot. The audit sample composition should be varied among the lots in order to estimate the precision and the accuracy at various concentrations and to prevent recognition of the audit samples by the analytical laboratories.

It was recommended that an empirical approach be used to calculate detection limits. Audit samples that have analyte concentrations near the expected detection limit should be measured, and it should be determined whether or not the analyte is reliably detected. Decision limits can be straightforwardly defined and accurately estimated from blank data alone.

The report by Permutt and Pollack (1986) was reviewed by the LEMSCo statistics staff (M. J. Miah, pers. comm.). For the purposes of the following summary, Permutt and Pollack are referred to as 'the authors' and M. J. Miah is referred to as 'the reviewer'. Page numbers cited are as listed in Permutt and Pollack (1986).

1. The authors describe the ELS-I field blank data as being non-normal (page 5) on the basis of a visibly skewed distribution and two apparently outlying observations (page 7). The reviewer states that this argument shows only evidence of possibly two outliers out of 245 observations in the field blank data; he recommends that statistical tests be performed to detect the outliers and the normality of the distribution.

2. The authors follow Hubbaux and Vos (1970) in their definition of the detection limit (page 10) as 'that true concentration for which the β quantile of measured concentrations is the decision limit'. The reviewer contends that the above definition contradicts other statements by the authors (specifically, the equality of α and β). The authors' definition of the detection limit also is found by the reviewer to contradict the definition by Long and Winefordner (1983) which is 3 times the standard deviation of blank sample measurements from a normally distributed population. The reviewer finds that "...the unverifiable assumption regarding the calibration curve is apparently redundant for the derivation of a nonparametric detection limit". He also finds that the formula presented on page 11 [$D = A + B$] is valid only if it assumed that the median of the blanks is at zero, and that since it is assumed that in blank sample measurements more values are positive than are negative, the assumption of a zero median is contradictory. An alternative proof for this relationship has been derived by the reviewer which is beyond the scope of this summary.

3. On page 16, the authors point out that measurement error variances are expected to be roughly proportional to concentration, and that "...it is therefore usual to report precision in the form of relative standard deviation (RSD)". The authors also use the root mean square (RMS) of % RSD to estimate the precision of duplicate measurements over a range of sample concentrations. The reviewer contends that, although the RMS of the absolute standard deviation is an unbiased estimator of σ, the RMS of % RSD is not a reliable estimator for $\sigma \div \mu$. The statistical derivation of the reviewer's proof for this statement is beyond the scope of the present summary. The Committee on Collaborative Interlaboratory Studies (1984) is recommended by the reviewer as source of mathematically straightforward, statistically defendable, and appropriate measures for estimating precision and accuracy.

4. The authors' use of an analysis of covariance to evaluate bias and trend is stated by the reviewer to depend on the assumption that measurement error variances are independent of concentration. However, the calculation of percent RSD requires the assumption that the measurement error variances are proportional to the concentration (page 15). Furthermore, the correction for bias and trend proposed by the authors involves fitting separate but parallel least-square lines for the two laboratories (page 24). The reviewer believes that applying a single slope to both laboratories imposes an artificial trend for at least one of the laboratories; he recommends that individual lines of best fit be applied to the data from each of the laboratories. The reviewer also recommends that the standard error rather than the standard deviation be used to estimate the precision of the corrected measurements.

5. The reviewer recommends that a mathematical model be developed which utilizes the ELS-I data and the data quality objectives as input parameters; a statistical evaluation could then be performed to determine whether the data quality objectives have been met.

In summary, the review of Permutt and Pollack (1986) finds criticism primarily with two of the assumptions that are used in the statistical evaluations: a zero median is assumed for blank sample measurements, and the measurement error variance is assumed to be independent of the analyte concentration for some purposes and to be proportional to concentration for other purposes. The other issues concern the evidence that was used to support the statement describing the blank sample data as non-normal, the use of the RMS for estimating the mean of %RSD values, the use of a single slope in correcting the bias and trend in audit sample data, the use of standard deviation instead of standard error to estimate precision in the corrected data, and the omission of the data quality objectives as a basis for the data quality evaluations.

SECTION 5

DATA VARIABILITY IN THE EASTERN LAKE SURVEY - PHASE I

Four types of precision estimates (overall within-batch, overall among-batch, analytical within-batch, and analytical among-batch) identify the amounts of data variability that can be attributed to sample collection, processing, storage, and analysis. For the ELS-I, each type of precision estimate was used to estimate a different aspect of data variability.

Overall within-batch precision (the total amount of data variability for samples collected and processed on a given day) was estimated by using field duplicate data. Analytical within-batch precision (the portion of the total data variability that occurred during chemical analysis of the samples collected and processed on a given day) was estimated by using laboratory duplicate data. The differences between the amounts of overall (field duplicate) and analytical (laboratory duplicate) within-batch precision indicate the amount of data variability that occurred during sample collection, processing, and storage.

Overall among-batch precision (total data variability among all sample batches) was estimated by using data from field natural audit samples and field synthetic audit samples. Analytical among-batch precision (the portion of the total among-batch variability that could be attributed to measurement imprecision including temporal effects) was estimated by using data from laboratory synthetic audit samples. The field natural audit samples were also used to provide an estimate of relative interlaboratory bias, and the field synthetic and laboratory synthetic audit samples were used to determine absolute interlaboratory bias and accuracy.

COMPARISONS OF PRECISION ESTIMATES

The four types of precision estimates are expected to relate in numerically consistent ways. By comparing the observed relationships between precision estimates to the expected relationships, the quality of the data can be evaluated. Quantitation limits (based on the variability of field blank and laboratory blank measurements) were used both for the evaluation of individual precision estimates and for comparing precision estimates.

The quantitation limits provided a means of classifying the data which was necessary to objectively evaluate precision. It is important to understand that the quantitation limit provided only two precision categories for each precision estimate (pairs with mean values greater than zero and pairs with mean values greater than the quantitation limit), whereas the relative precision may be expected to vary along the entire range of mean sample values. Therefore, if the sample concentrations in two populations are sufficiently different, the relative precisions of the sample populations will differ even when both populations have mean values above a quantitation limit. Such differences may be unimportant when, for example, the precision estimates for both populations meet predetermined precision goals. ELS-I data quality was evaluated by comparing the relative variability of samples which had means above the quantitation limits against the DQOs established prior to the survey. When precision is expressed in absolute terms (as it was for pH in the ELS-I), the observed precision can be directly compared against the DQOs.

The inherent differences between the methods used to calculate precision estimates should also be considered when comparing chemical measurements from the ELS-I. Precision estimates for many samples that have the same concentration (e.g., among-batch precision using audit samples) can be expressed in terms of the percent relative standard deviation (%RSD). Among-batch precision estimates were therefore directly comparable with the interlaboratory precision goals which were part of the DQOs. Precision estimates for measurements that have a wide range of values (e.g., field duplicate pairs and laboratory duplicate pairs) can be calculated as the root mean square (RMS) of %RSD. The RMS of %RSD estimates the mean of the %RSD over the observed range of mean sample pair values. Because the RMS of %RSD is an estimate of the true %RSD, the within-batch precision values from survey data are directly comparable to the interlaboratory precision goals as set forth in the DQOs for the ELS-I.

EXPECTED RELATIONSHIPS BETWEEN PRECISION ESTIMATES

Overall within-batch precision estimates were expected to be numerically larger than analytical within-batch precision estimates by an amount equal to the variability from sample collection, processing, and storage (see above). Similarly, overall among-batch precision estimates were expected to be numerically larger than analytical among-batch precision estimates. Analytical and overall among-batch precision estimates were expected to be numerically larger than the corresponding analytical and overall within-batch precision estimates by amounts that were equal to the temporal variability.

The exceptions to the four types of expected relationships between precision estimates in the ELS-I are listed below. Unless specifically noted, the comparisons which include overall or analytical within-batch precision estimates are based on duplicate pairs with means greater than the quantitation limits. Where the mean of the audit sample values for total extractable Al or total Al were less than 0.010 mg L^{-1}, the among-batch precision estimates for those measurements were compared to the corresponding within-batch precision estimates for duplicate pairs with means less than 0.010 mg L^{-1}. Similarly, where the mean of audit sample DOC values was less than 5.0 mg L^{-1}, the among-batch precision for those measurements was compared to the corresponding within-batch precision estimate for the duplicate pairs which had means less than 5.0 mg L^{-1}. This convention was also followed for the comparisons between precision estimates for Al and DOC means which were greater than 0.010 and 5.0 mg L^{-1}, respectively.

Overall within-batch precision estimates were numerically larger than analytical within-batch precision estimates for all parameters except total extractable Al, conductance, Mn, total P, and SO_4^{-2} (see Tables 23 and 24).

Overall among-batch precision estimates from FN2 audit samples were numerically larger than overall within-batch precision estimates for all parameters except total dissolved F^-, NO_3^-, initial ANC pH, and initial BNC pH (see Tables 22 and 25). This relationship was observed for both FN2 samples with means greater than the quantitation limits and for FN2 samples with means less than the quantitation limits. Overall among-batch precision estimates from FN3 audit samples were numerically larger than overall within-batch precision estimates for 15 of 23 parameters (see Tables 22 and 25). Exceptions to this relationship include values for ANC, Cl^-, conductance, air-equilibrated DIC, total dissolved F^-, NO_3^-, air-equilibrated pH, and SO_4^{-2}. Overall among-batch precision estimates from FH audit samples were numerically larger than overall within-batch precision estimates for all parameters except NH_4^+, NO_3^-, and SO_4^{-2} (see Tables 22 and 26). Overall among-batch precision estimates from FL audit samples were numerically larger than overall within-batch precision estimates for all parameters except total Al, ANC, Mn, and NH_4^+ (see Tables 22 and 27). Lastly, analytical among-batch precision estimates from both LH and LL audit samples were numerically larger than analytical within-batch precision estimates for all parameters except conductance, Mn, and SO_4^{-2} (see Tables 24, 26, and 27).

Exceptions to the expected relationships were generally associated with the presence of one or more extreme outliers in the verified data set, with values close to the detection limit, or with a methodological problem. Many exceptions involved small differences in estimated precision. In several cases it was necessary to retain confirmed but questionable values in the verified data set which were later deleted during data validation. The confirmed, questionable values influenced the statistical evaluation of the ELS-I data. For subsequent surveys, a data qualifier (XO) was added to ensure that such values were retained in the verified data set but were not included in statistical calculations.

This brief discussion of the discrepancies in the expected ELS-I precision relationships is a first step in understanding the mechanisms that affect data variability. A more comprehensive analysis of these discrepancies is needed to adequately describe the potential contributing factors and their implications. The complexity of such an analysis is a subject which calls for detailed evaluation in a separate report.

SECTION 6

SUMMARY

In general, the ELS-I was conducted smoothly and efficiently with surprisingly few problems given the magnitude of the survey. This success may be attributed to the use of a peer-reviewed research plan, a QA plan, and operations, training, and methods manuals, as well as to the efforts of all of the individuals involved. When problems did occur, they were identified and generally resolved quickly; this indicates that the checks and balances fundamental to the QA program operated effectively. The operational QA program appeared to be adequate to ensure that all samples were collected and analyzed consistently and that the resulting data were of known and traceable quality.

PILOT STUDY

Implementation of pilot studies prior to the ELS-I proved to be worthwhile in that many field sampling and analytical issues which could have caused problems during the full survey were corrected without loss of survey data. In particular, a nitrate contamination problem was identified and partially resolved prior to initiation of the survey.

FIELD OPERATIONS

The field QC and calibration procedures proved sufficient to detect specific instrument or operator problems; this was evidenced by detection of both a faulty pH meter and contamination of field blanks which was caused by the use of deionized water from a supply not meeting ELS-I requirements. The equipment-washing procedure used by the field laboratory personnel was modified midway through the survey to eliminate the remainder of the nitrate contamination problem.

ANALYTICAL LABORATORY OPERATIONS

Analytical QC procedures were also sufficient as evidenced by the detection and resolution of both a silica calibration error and of aluminum contamination which resulted from the use of borosilicate glassware and from floor sanding. The analytical laboratories were able to produce acceptable nitrate data for samples processed before the nitrate contamination source was identified and eliminated by analyzing for nitrate in aliquot 5 as well as in aliquot 3.

DATA BASE AND VERIFICATION OPERATIONS

The data base entry and verification procedures enabled virtually all transcription, transposition, and typographical errors on the various forms to be detected and corrected. The use of the tuple system to correct errors was slow because of the number of times that the correction process had to be iterated; the alternative method that was employed was labor-intensive. Different correction procedures were implemented for later surveys.

EVALUATION OF QUALITY ASSURANCE AND QUALITY CONTROL DATA

Evaluation of the QA and QC sample data indicated that the data quality objectives for detectability and precision were achievable. The importance of using field blank measurements during data interpretation was demonstrated.

Little bias was detected among field stations and analytical laboratories relative to the imprecision of the measurements. Evidence was presented to show that the bias that did exist could be quantified and that correction factors could be applied to the values to aid in data interpretation (see Appendix A). In future surveys, the synthetic audit samples should have a wider range of analyte concentrations to assure that variability will be properly assessed at all concentration levels likely to be encountered in lake samples.

CONCLUSION

These results point to the usefulness of the QA program in assuring consistency and reliability of the data collected in the NSWS. To that end, the ELS-I QA program was successful in producing data of known and verifiable quality in accordance with the objectives of the NSWS.

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APPENDIX A

ANALYSIS OF QUALITY ASSURANCE DATA FOR THE EASTERN LAKE SURVEY

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The following document is a final report on the statistical evaluation of quality assurance data for the ELS-I which was prepared for Lockheed-EMSCO.

Final Report

ANALYSIS OF QUALITY ASSURANCE DATA FOR THE EASTERN LAKE SURVEY

SYSAPP-86/040

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NOTICE

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1 INTRODUCTION

The National Surface Water Survey, designed and begun by the U.S. Environmental Protection Agency in cooperation with the National Acid Precipitation Program, is a three-phase project intended to document the chemical and biological condition of lakes and streams considered susceptible to the effects of acidic deposition. Phase IA of the program is a survey of lake chemistry. It consists of the Eastern Lake Survey, with which this report is concerned, and the Western Lake Survey, which is currently underway. The primary objectives of the phase IA survey are to determine how many lakes have low pH or alkalinity in regions of the United States potentially sensitive to acidic deposition and to understand the chemical composition of these lakes. From the lakes sampled in phase IA some will be selected for intensive study in phases II and III of the project (EPA, 1984).

Four regions of the United States were selected for study in phase IA: the Northeast, the Southeast, the upper Midwest, and the mountainous West. These regions were chosen because they are known to contain an abundance of low-alkalinity lakes, which are considered sensitive to acidic deposition. The Eastern Lake Survey covered the Northeast, Southeast, and upper Midwest regions and was completed in late 1984.

The sampling plan is a stratified design. Each region is divided into subregions, and within a subregion lakes are divided into three alkalinity classes. In addition, there are minor stratification variables: lake size, elevation, and watershed size. An extensive quality assurance/quality control (QA/QC) program was designed and carried out to assure high-quality data and to identify any problems in the collection, processing, and analyzing of the lake water samples (Drousé et al., 1985). While the primary purpose of the QA/QC data was to identify and correct potential data quality problems during the survey, they also serve to assess the data quality that was achieved, which is the subject of this report.

Two-liter lake samples were collected by helicopter crews and processed by one of eight field laboratories. At the field laboratories the samples were split into seven aliquots, labeled (by coded identification number, not by lake name), and shipped to one of four contract laboratories for chemical analysis. Each field laboratory was supposed to send all of its samples (audit and routine) to one contract laboratory, but this protocol was not always maintained. Four contract laboratories analyzed the lake samples: EMSI analyzed samples collected by four of its field laboratories from 8 October to 7 November 1984; Versar analyzed samples collected by two of its field laboratories and two of EMSI's field laboratories from 7 October to 16 November 1984; Global analyzed samples collected by its field laboratory and two of Versar's field laboratories from 20 October to 29 November 1984; and one U.S. Geological Survey field laboratory collected samples after all other field laboratories completed their sampling, from 2 December to 14 December 1984.

The sample load for a field laboratory was restricted to 24 routine lake samples per day. A batch is defined as the set of samples collected by a single field laboratory on a single day (i.e., 24 routine samples per batch). Each batch was identified by a three-digit code. Over the duration of the Eastern Lakes Survey, a total of 127 batches were analyzed. One duplicate sample was obtained at one lake (usually the first) sampled in each batch.

Each lake was visited only once during the survey and each sample was processed by one field station and one contract laboratory. Consequently, some important aspects of the quality of the data cannot be judged from the routine data themselves. Systematic differences between laboratories could result from minor differences in instrumentation or procedure or from real differences between the sets of lakes measured by the different laboratories. Similarly, variations among measurements by one laboratory could reflect real differences between lakes or simply the imprecision of the measurements. The routine data do not allow these possibilities to be distinguished. The quality assurance data, however, make it possible to estimate the likely magnitudes of various kinds of error. Variations larger than these in the routine measurements may confidently be supposed to represent actual differences between lakes.

Several kinds of blind QA samples are used to estimate the components of the error in the whole system from collection to analytical determination. For one, there are duplicates of the routine samples. These duplicates are of two types, called field and laboratory duplicates. Field duplicates are second samples collected from one lake in each batch and processed in parallel with the routine samples. Laboratory duplicates are splits made at the analytical laboratories so that the analysis, but not the routine sample processing, is duplicated. Both types of duplicate measurements indicate, by the difference between the measurements of a pair, the repeatability of measurements by a given laboratory on a given day. The laboratory duplicates indicate the the repeatability of the analytical determination alone, the field duplicates indicate the repeatability of the entire system of measurement from collection to analysis. Neither type tells us anything about variation across laboratories or across days, such as would be produced by errors in calibration.

For this we have the natural and synthetic audit samples. Natural audit samples were prepared daily from stored lots of water originally collected from Big Moose Lake in the Adirondacks and Lake Superior. Synthetic audit samples were prepared daily by diluting concentrate lots of known composition. There are both field and laboratory synthetic audits: field synthetic audits were shipped to the field stations in two-liter containers and were divided into aliquots at the field stations, whereas laboratory synthetic audits arrived at the field stations ready for reshipment to the contract laboratories and thus skipped the processing at the field stations. The natural audits are field audits. These samples thus furnish repeated measurements of the same thing, by the same and by different laboratories, assuming stability of the natural audits in storage and consistency in preparation of the synthetic audits. Unlike the duplicates, therefore, they give information about relative bias between laboratories and about reproducibility of measurements from day to day. In addition, there is some independent information about what is in the synthetic audit samples, namely the recipes for them. Unfortunately, this information turns out to be very unreliable.

The quality assurance plan also provided for blank samples to reveal any problems of contamination and also study the detectability of analytes at low concentrations. There were laboratory blanks, which are not discussed in this report, and field blanks, which were samples of deionized water processed at the field stations like routine samples.

This report discusses methods we developed for estimating measurement errors from the quality assurance data as well as the results. We consider first the evaluation of detectability from field blank data, then the analyses of duplicate data and natural and synthetic audits. Our work is concerned with 24 parameters measured by the contract laboratories. Mineral acidity and carbonate alkalinity were not analyzed because most of the measurements were missing or considered unreliable. Nitrate is included, but it is being studied in much greater detail by Liggett (1985).

2 DETECTION LIMITS

For the purpose of evaluating the detectability of various parameters at low levels, the quality assurance plan for the Eastern Lake Survey provided for some 245 field blank samples. A Van Dorn sampler was filled with deionized water, and aliquots were prepared at the field stations in the same way as routine samples. The blank samples were then shipped to the contract laboratories along with routine samples. The labels were coded so that the laboratories were blind as to which samples were blank.

Because the field blank samples were processed as much like the routine samples as possible, measurements of the blanks are subject to errors from all the sources that affect the routine measurements. Internal blanks within the contract laboratories were also measured and used to calculate instrument detection limits. These instrument detection limits are unlikely to be achieved in routine samples because the internal blanks are immune to three kinds of error that affect routine (and field blank) measurements. First, the internal duplicates are not analyzed blind, and analyses of samples known to be blanks may be expected to have rather less variable results than blind analyses. Second, the field blank samples, like the routine samples, are exposed to varying degrees of contamination in processing before they reach the laboratory, whereas the internal blanks are not. Third, errors in calibration of an instrument do not affect the calculated instrument detection limit. The instrument detection limit may be calculated from the standard deviation of 10 measurements of internal blanks on the same day. If the calibration is wrong that day, the mean, but not the standard deviation, will be affected. In contrast, the field blanks are analyzed on many different days, and so variation in field blanks reflects errors in calibration.

Our definitions and method of calculating system detection and decision limits from measurements of field blanks follow in spirit those of Hubaux and Vos (1970). The details are different for a number of reasons. Hubaux and Vos were concerned with allowing for calibration error when the measurements are all from one calibration; we are not because the measurements are from many calibrations so that their variation includes calibration error. They were also concerned with allowing for uncertainty about the long-run distribution of measurements of blanks when only a few blanks are measured; we are not because there are 245 field blanks. On the other hand, by using nonparameteric techniques, we are able to dispense with their assumption that measurements have normal distributions. This is fortunate because the field blank data clearly do not follow normal distributions.

Following Hubaux and Vos, we distinguish two kinds of limits: decision limits and detection limits. We also calculate a third kind of limit, sometimes called a quantitation limit. The decision limit is a measurement that reliably indicates a level above background. The detection limit is a concentration that would probably be detected if that concentration were present. The quantitation limit is a concentration that can be measured with reasonable precision. These concepts are explained in turn below.

DECISION LIMITS

We define the decision limit, following Hubaux and Vos, as "the lowest signal that can be distinguished from the background." It is thus a measurement so high that it rarely occurs in blank samples. If this high a measurement does occur, it is therefore a more or less reliable indication that the sample is not a blank; the more rarely such a measurement occurs in blanks, the more reliable an indication it is. If the decision limit is set at the upper α quantile of the distribution of blanks, a measurement above the decision limit can be said to be significantly different from background at level α. This means that the probability of erroneously calling a measurement significant that is really background is only α.

It remains only to choose an error rate α that we are willing to accept and then to estimate the upper α quantile of the background distribution. Provided α is not too small (at least several times 1/245), we can estimate the quantile simply, by the observed quantile of the 245 measurements. For example, for $\alpha = .05$, the decision limit is taken to be the 95th percentile of the measurements of blanks. Measurements higher than this occur only 5 percent of the time for blank samples, so such a measurement is a significant indication (at the .05 level) that the sample in question is not a blank.

There is no consensus on what the probability of error α should be. It might seem desirable to make α very small, perhaps a fraction of 1 percent. This approach has two drawbacks. First, it is impossible to reliably estimate very high quantiles without very many observations. For example, suppose that a certain kind of error, say an unusual contamination, affected one sample in 100 and that decision limits were based, as they often are, on sets of 10 samples. Suppose that the decision limit was to be the 99th percentile. In nine out of every 10 sets of 10 samples, none of the samples would be affected by the unusual error, so that the 99th percentile would be underestimated. In one out of 10 sets, a measurement would be affected, and then such an error would be assumed to happen in about one out of 10 measurements; the 99th percentile would thus be overestimated. Quite simply, we get a very poor idea of what happens in one out of 100 measurements (the 99th percentile) by looking at 10 measurements.

Second, even when there are enough measurements to estimate a very high quantile, it may not be desirable to do so. To continue the example, with 245 observations we are likely to see two or three of those unusual errors. The 99th percentile of the 245 measurements will therefore probably be one of those unusual measurements. The question is, do we want the reported decision limit to reflect this rather extreme behavior of the measuring process at its worst, or somewhat more typical behavior? Our answer is, the more typical behavior. Accordingly, we use the 95th percentile of the measurements of blanks as the decision limit. Any measurement above our calculated decision limit is thus significantly different from background at a significance level (or error rate) of $\alpha = .05$.

It is usual to calculate a decision limit from the mean ($\overline{X}$) and standard deviation of the measurements of blanks. For example, the decision limit might be taken to be $\overline{X} + 3$ s and the detection limit, which will be discussed later, 6 s. More commonly, 3 s is used as the detection limit, and this corresponds to a decision limit of $\overline{X} + 1.5$ s. So defined, the decision limit can be calculated from very few measurements, even as few as two. However, such a definition has two serious disadvantages. First, it is impossible to know the error rate. The measurements are sometimes assumed to follow a normal distribution; if they did, $\overline{X} + 1.5$ s would be about the 93rd percentile and the error rate would be about 7 percent. Unfortunately, the validity of this assumption cannot be checked unless there are so many measurements that the assumption is unnecessary. On the other hand, even if the distribution is not normal, Long and Winefordner (1983) point out that a mathematical result called Chebyshev's inequality limits the error rate. Unfortunately, the limit is crude: anywhere from none up to 4/13 of a distribution can be at least 1.5 standard deviations above the mean.

The second disadvantage of basing the decision limit on the mean and standard deviation is that these statistics are very sensitive to outliers. If there are a few very high measurements, the standard deviation in particular may be more heavily influenced by these few than by all the rest. Here again, the decision limit would reflect the extreme rather than the typical behavior of the system. Nevertheless, in addition to the

95th percentile, for purposes of comparison we calculate a decision limit as 1.5 standard deviations above the mean of the measurements of blanks.

The case of sulfate illustrates all these points. Figure 2-1 summarizes the 245 measurements of sulfate in field blanks. The distribution is very skewed to the right; it does not look like a normal distribution at all. The highest value (2.61 mg/l), is more than eight times the second highest (0.31 mg/l), which is in turn twice the third highest (0.16 mg/l). The mean is 0.043 mg/l and the standard deviation is 0.17 mg/l. Both are heavily influenced by the outliers: eliminating just the one largest measurement would reduce the mean to 0.032 mg/l and the standard deviation to 0.034 mg/l. The 95th percentile is 0.093 mg/l. There are several measurements fairly close to that above and below; the nearest are 0.085 and 0.094 mg/l. On the other hand, 1.5 standard deviations above the mean is 0.30 mg/l; this would be the 93rd percentile of a normal distribution, but it is above the 99th percentile for this distribution. There is only one measurement anywhere near 0.30 mg/l, and only one other that is higher. Thus the $\overline{X} + 1.5\ s$ decision limit mainly reflects the two largest measurements out of 245.

Table 2-1 shows the system decision limits for all parameters (except pH) analyzed by the contract laboratories, as well as the detection limits, which we discuss next. Both the parametric version based on mean and standard deviation and the nonparametric version we recommend are shown.

DETECTION LIMITS

Hubaux and Vos call a detection limit "the limit at which a given analytical procedure may be relied upon to lead to detection...." "Detection" here can be understood to mean a measured concentration above the decision limit, for if the measurement is above the decision limit it can be reliably asserted that the analyte is present in more than background amounts, i.e., that it has been detected. The question thus becomes, how high does the true concentration have to be before the measured concentration can be relied on to be above the decision limit? If D is the detection limit, then when the true concentration is D, the measured concentration should be above the decision limit except with some small probability β. Thus, two kinds of error are relevant to the definition of a detection limit. First, false detection occurs when the measurement is above the decision limit but the sample is in fact a blank. The decision limit was chosen to limit the probability of this kind of error to α. Second, failure to detect occurs when the sample is not a blank but the measurement is below the decision limit. The higher the true concentration, the less probable is this kind of error. The true concentration at which the probability is just β is the detection limit.

```
                    MOMENTS                                            QUANTILES(DEF=3)                                        EXTREMES
N                245  SUM WGTS           245        100% MAX      2.61      99%        0.15                  LOWEST    HIGHEST
MEAN       0.0426653  SUM             10.453         75% Q3      0.046      95%       0.093                  -0.023      0.137
STD DEV     0.168075  VARIANCE     0.0282494         50% MED      0.03      90%       0.066                  -0.023      0.142
SKEWNESS     14.7423  KURTOSIS        225.66         25% Q1       0.01      10%           0                  -0.023       0.15
USS          7.33883  CSS            6.89285          0% MIN    -0.023       5%      -0.004                   -0.02       0.31
CV           393.939  STD MEAN     0.0107379                                 1%      -0.023                   -0.02       2.61
T:MEAN=0     3.97332  PROB>|T|        0.0001        RANGE        2.633
SGN RANK       11800  PROB>|S|        0.0001        Q3-Q1        0.036
NUM ^= 0         223                                MODE          0.03
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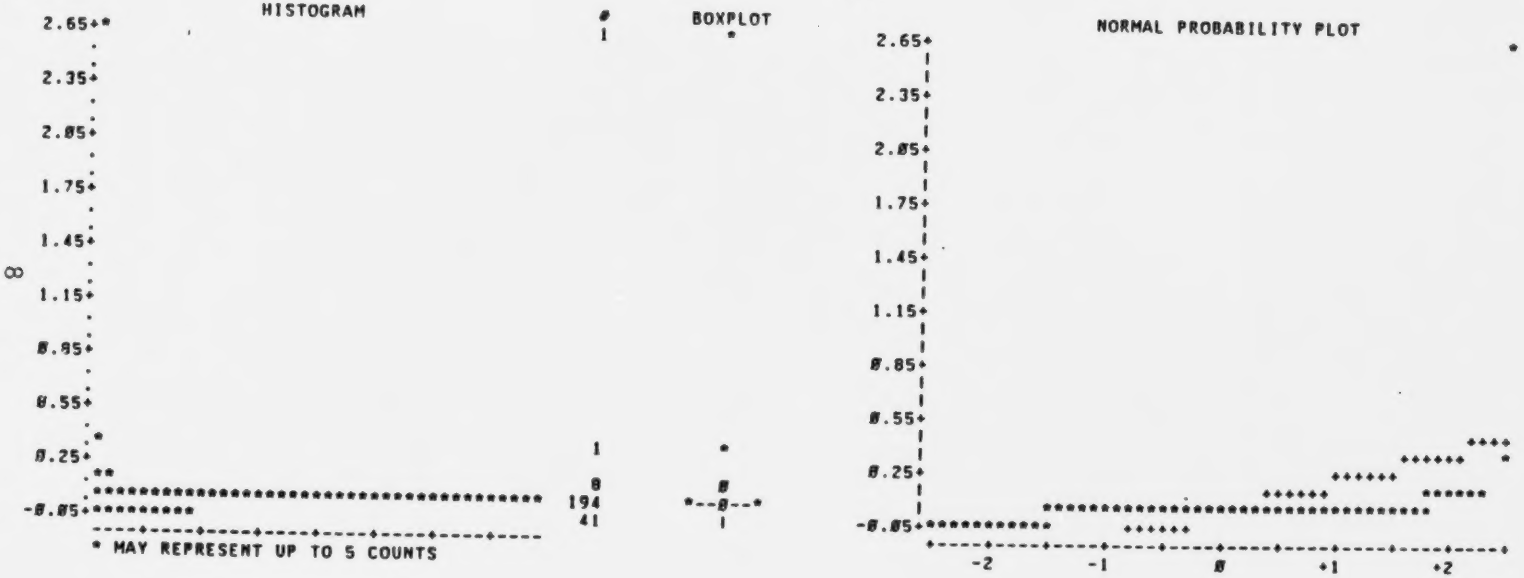

FIGURE 2-1. Summary of sulfate measurements of 245 field blanks.

TABLE 2-1. System decision and detection limits.

Parameter*	System Detection Limit		System Decision Limit		Quantitation Limit (10 s)
	Parametric (3 s)	Nonparametric ($2(P_{95} - P_{50})$)	Parametric ($\overline{x} + 1.5$ s)	Nonparametric (P_{95})	
Calcium	0.043	0.060	0.026	0.030	0.15
Magnesium	0.012	0.016	0.007	0.008	0.039
Potassium	0.11	0.032	0.062	0.017	0.37
Sodium	0.060	0.056	0.037	0.028	0.20
Manganese	0.028	0.022	0.016	0.011	0.093
Iron	0.037	0.044	0.020	0.022	0.12
Aluminum (extractable)	0.012	0.014	0.008	0.008	0.039
Chloride	0.11	0.13	0.083	0.080	0.39
Sulfate	0.52	0.13	0.29	0.093	1.7
Nitrate	1.0	0.76	0.60	0.39	3.4
Silica	0.70	0.21	0.35	0.11	2.3
Fluoride (total)	0.010	0.008	0.007	0.005	0.034
DOC	0.76	0.44	0.59	0.41	2.5
Ammonium	0.17	0.056	0.098	0.038	0.56
Acidity (µeq/l)	45	18	33	22	150
Alkalinity (µeq/l)	17	11	9.9	6.9	57
Conductivity (µS/cm)	2.8	1.4	1.8	1.3	9.0
DIC (equilibrated)	0.17	0.20	0.27	0.28	0.56
DIC (initial)	0.33	0.38	0.41	0.42	1.1
Phosphorus (total)	0.011	0.014	0.007	0.008	0.037
Aluminum (total)	0.084	0.050	0.051	0.030	0.28

* All parameters measured in mg/ℓ unless otherwise noted.

The detection limit thus depends on the decision limit and, through it, on the distribution of measurements of blanks. The detection limit also depends on the distribution of measured concentrations for various small, positive true concentrations: in fact, the detection limit is that true concentration for which the β quantile of measured concentrations is the decision limit. Unlike the distribution of blanks, the distribution of measurements at the detection limit has not been observed. To observe it would require audit samples with true concentration equal to the detection limit, and to get these entails knowing the detection limit in advance. Instead, the distribution at the detection limit must be inferred from the distribution of blanks.

Let us therefore look again at the distribution of sulfate measurements in blanks, which was presented in Figure 2-1. Some new points are now of interest. The observations are mostly positive: 91 percent are more than zero, the median is 0.030 mg/l, and the mean is 0.043 mg/l. There are two reasons for this result. First, while the field blank samples start out as deionized water, they go through the same processing as the lake samples before they get to the laboratory and thus may be contaminated in the process. It is likely that many blanks actually do contain measurable amounts of sulfate by the time they are analyzed. Second, the measurement error for a blank sample is very likely to be positive. It is not impossible to measure a concentration as negative because of the calibration of the instrument: if an unknown produces a signal less than that of the calibration blanks, the measured concentration is negative. Still, errors are much more likely to be positive than negative: there are many ways to overestimate a concentration that is nearly zero, and not many ways to underestimate it. Furthermore, even when the calibrated instrument produces a negative reading, this reading might not appear in the reported data: it might be recorded as zero, or the instrument might be recalibrated and this reading might be discarded.

These effects on the distribution of blanks are important precisely because the distribution of measurements at the detection limit is not likely to be affected in quite the same way. Suppose that the true concentration of sulfate in a lake sample is some small positive amount x and that this sample is measured many times. What does the distribution of these measurements look like? It is reasonable to assume that contamination affects this sample the same way it affects blanks since contamination simply adds sulfate to the sample, no matter how much was in it to start with. (This would not be reasonable for parameters that are not additive, e.g., conductivity.) However, it is not reasonable to assume that measurement error affects this sample the same way it affects blanks. Along with positive errors, negative errors of up to x are now possible, and if most errors are smaller than x, negative and positive errors will be about equally likely. Furthermore, the reporting problems with negative measurements will have little effect since there are few negative measurements: only an unusually large (more than x) negative error produces a negative measurement. On the other hand, the upper part of the distribution of measurements of this sample might resemble that for blanks, shifted by x, since the sources of positive errors are the same.

As x moves away from zero, then, the shape of the lower half of the distribution changes. The lower half is likely to look more and more like a mirror-image of the upper half. The upper half keeps about the same shape as for $x = 0$, a blank.

The problem is to find an x for which the lower β quantile of the distribution is the decision limit. With a true concentration of x, the measurements will be above the decision limit except with probability β, and so the analyte will be "detected" with probability $1 - \beta$. This is the detection limit.

Figure 2-2 shows a solution. It is assumed that in the distribution of measurements at true concentration D, the half above the median is the same as the upper half of the distribution of measurements of blanks, but shifted by D. The lower half is a mirror-image. The detection limit D is the sum of A, the distance from the median of measurements of blanks to the decision limit, and B, the distance from the lower β quantile to the median at true concentration D. By symmetry, B equals C, the distance from the median to the upper β quantile, and by assumption, this distance is the same at D as for blanks. Under these assumptions, the decision limit can be calculated from the distribution of measurements of blanks as

$$\begin{aligned} D &= A + B \\ &= A + C \\ &= (q_\alpha - q_{.5}) + (q_\beta - q_{.5}) \end{aligned}$$

where q_α and q_β are the upper α and β quantiles and $q_{.5}$ is the median. We use $\beta = \alpha = .05$, giving a detection limit of $2(P_{95} - P_{50})$, i.e., twice the difference between the 95th percentile and the median of the measurements of blanks.

As with decision limits, it is more usual to calculate detection limits from the standard deviation of the measurements of blanks. The detection limit is often reported as 3 s, where s is the standard deviation. This may be taken to correspond to our procedure with a decision limit of $\bar{X} + 1.5$ s, where $\bar{X}$ is the mean, and with the mean replacing the median. The error rates, assuming a normal distribution, would be $\alpha = \beta = .07$. Of

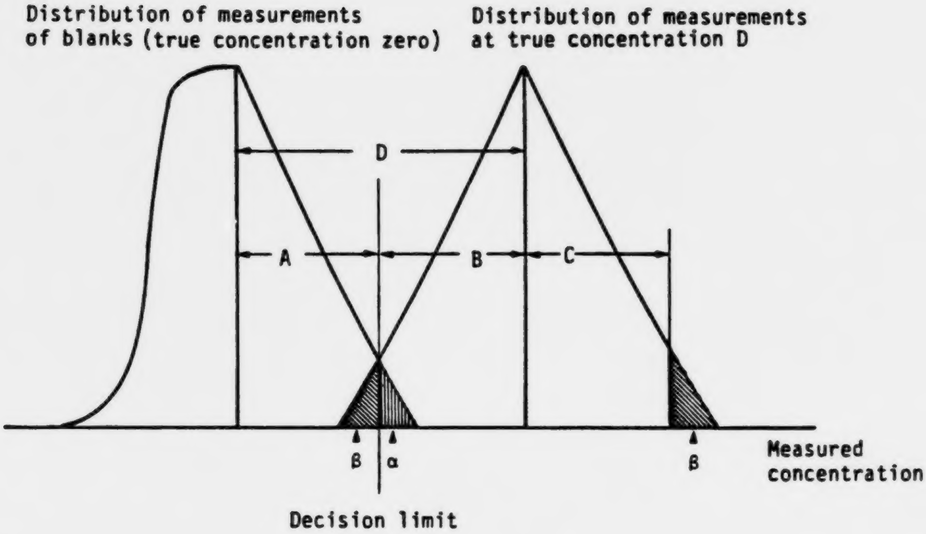
Distribution of measurements of blanks (true concentration zero)
Distribution of measurements at true concentration D
D
A
B
C
β
α
β
Measured concentration
Decision limit

FIGURE 2-2. Calculation of the detection limit (D). See the text for discussion.

course the same detection limit gives different combinations of α and β with different decision limits. For example, with $\bar{X} + 3$ s as the decision limit and 3 s as the detection limit, and still assuming normality, $\alpha = 0.003$ but $\beta = 0.5$, which can hardly be called reliable detection.

Basing detection limits on the standard deviation has the same disadvantages as apply for decision limits. The standard deviation is very sensitive to outliers. Since the distributions are not normal, the error rates cannot be known. In addition, to assume normality is to assume the same distributional shape for blanks and nonblanks; but, as we have argued, the one is skewed and the other may be almost symmetric. Still, we compute a 3 s detection limit for purposes of comparison.

For parameters that are not additive, like conductivity, the interpretation of the detection limit is a little complicated; indeed, the concept of detection limits may not be very useful for conductivity. Conductivity different from that of a blank will be detected reliably if the conductivity of the sample exceeds that of a blank by more than the detection limit. For concentrations, on the other hand, the difference between the true concentration when measured and the background added in processing is simply the true concentration in the sample to begin with. So the interpretation for concentrations is more straightforward: a concentration that is above the detection limit before processing will be detected reliably. The detection limits for all chemical parameters (except pH) analyzed by the contract laboratories are given in Table 2-1. Again we show both the traditional detection limit based on standard deviation and the nonparametric version we recommend.

QUANTITATION LIMITS

If the true concentration is at the detection limit, the measured concentration will probably be above the decision limit: this is how those two limits were chosen. However, if the median background concentration is small, the decision limit is only about half the detection limit. So negative relative errors of as much as 50 percent will occur with probability β in measuring such low true concentrations. Smaller relative errors are expected at higher true concentrations. If the absolute standard deviation were the same as for blanks, the relative standard deviation would be more than 10 percent for any true concentration up to 10 s and less than 10 percent for any above 10 s. This is only saying that s is more than 10 percent of any number up to 10 s, which has sometimes been called the limit of quantitation (e.g., by Long and Winefordner, 1983). We use it in the next section in computing estimates of precision: samples believed to have true concentrations below the quantitation limit are excluded from estimates of precision since high precision is not expected at such low concentrations. Quantitation limits are shown in Table 2-1.

3 DUPLICATE SAMPLES

INTRODUCTION

At one lake each day, usually the first, each helicopter crew collected a second sample. This duplicate sample was processed by the field station in the usual way and shipped to the contract laboratory with a label coded so that it was indistinguishable from the routine samples in the batch. Differences between measurements of these field duplicate samples reflect analytical error and also errors at the lake and at the field station. For example, the sampling procedure might vary slightly from one sample to the next, or one of the samples might be contaminated in preparing the aliquots at the field station.

In addition, duplicate samples in each batch were created at the contract laboratory by splitting one sample. Differences in measurements of these laboratory duplicates reflect only analytical errors at the contract laboratory, and only variation within a batch and not from day to day. For example, unless the instrument is recalibrated within the batch, any error in calibration will not be seen as a difference within a duplicate pair.

Field and laboratory duplicate pairs are thus quite different in origin and provide information on different aspects of data quality. Nevertheless, the form of the data is the same--pairs of measurements of the same thing. Our method of analysis is also the same for both, and so we discuss them together here.

METHOD

Since the analysis is simplest for the three measurements of pH by the contract laboratories, we begin there. Errors in pH measurements are believed to be about the same size for any pH over the relevant range; in any case, since pH is already a logarithm, there is no point in taking relative standard deviations. The standard deviation of each duplicate pair is

$$s = \left[\left(R - \frac{R + D}{2}\right)^2 + \left(D - \frac{R + D}{2}\right)^2\right]^{1/2}$$

which can be written more simply as

$$s = |R - D|/\sqrt{2}$$

where R and D are the routine and duplicate measurements. Now the question arises of how to combine the standard deviations for duplicate pairs to get an estimate of precision. According to statistical theory, the right summary statistic is the pooled or root-mean-square standard deviation

$$\text{RMS standard deviation} = \left(\frac{1}{n} \sum s_i^2\right)^{1/2} ,$$

where n is the number of pairs.

To show the different effects of using this and other summary statistics for the standard deviation, we did a Monte Carlo experiment. Consider an imaginary lake with pH 5.08 and measurements of pH subject to errors normally distributed with mean zero and standard deviation 0.03. (Actually, this approximately describes Big Moose Lake in the natural audit measurements.) We drew 10 sets of 100 pairs of samples from such an imaginary lake. We calculated the standard deviation of each pair, and then we computed four summary statistics for the 100 standard deviations in each set: the root mean square (RMS), the mean, the median and the geometric mean. The results are shown in Table 3-1. As we would expect from statistical theory, the 10 root mean squares are clustered around the actual measurement error of 0.03, and all three other summary statistics are systematically too small.

For parameters other than pH there are two complications. First, errors are expected to be roughly proportional to concentration, at least at high concentrations. It is therefore usual to report precision in the form of relative standard deviation (RSD). We calculate RSD for each duplicate pair by dividing its standard deviation by its mean, and again we use root mean square as a summary statistic for RSDs. Second, the proportional relationship breaks down at very low concentrations: as concentration approaches zero, measurement error does not vanish. Therefore, RSDs may be very high at low concentrations. What is of interest is the RSD at concentrations that are not extremely low. We therefore compute the RMS RSD for pairs with mean greater than the quantitation limit, defined as 10 times the standard deviation of measurements of field blank samples.

We note that the theoretical argument for using the RMS of RSDs, unlike standard deviations, is only approximate. However, the approximation is

TABLE 3-1. Various summary statistics for the standard deviation of duplicate pairs in a Monte Carlo experiment.

RMS	Mean	Median	Geometric Mean
0.030	0.024	0.020	0.018
0.027	0.022	0.019	0.014
0.029	0.024	0.021	0.017
0.033	0.026	0.025	0.017
0.030	0.025	0.020	0.017
0.031	0.024	0.020	0.017
0.030	0.024	0.020	0.017
0.031	0.025	0.021	0.018
0.030	0.024	0.019	0.016
0.026	0.022	0.024	0.016

Ten sets of 100 duplicate pairs are represented. All 2000 measurements have a normal distribution with mean 5.08 and standard deviation 0.03. The standard deviation of each pair was calculated, and then four summary statistics were calculated for the 100 standard deviations in each set.

standard, and it is reliable whenever RSDs are much less than 1 (100 percent), which is the case here. Use of the RMS RSD has been recommended by the Environmental Protection Agency for its QA work (EPA, 1983).

RESULTS

Table 3-2 shows the estimates of precision for the three pH parameters. As expected, the figures for field duplicates are slightly higher than those for laboratory duplicates, reflecting some variability in the field procedure or perhaps some real difference in the pH of water collected in successive samples. Most of the variability is already present in laboratory duplicates, however, and so must be attributed to analytical imprecision.

Tables 3-3 and 3-4 show the estimates of relative precision of measurements other than pH from field and laboratory duplicate pairs. The precision (RMS RSD) is calculated for all pairs with a positive mean measured concentration and for just those pairs with a mean above the quantitation limit. Again, the estimates from field duplicate pairs are generally a little higher than those from laboratory duplicate pairs, as expected. Extractable aluminum, sulfate, conductivity, and phosphorus are exceptions.

The estimates of precision from laboratory duplicate pairs for half a dozen parameters, including all these exceptions, are each heavily influenced by a single very high RSD. Table 3-5 identifies these outliers and shows the RSD recalculated when they are eliminated.

TABLE 3-2. Within-batch precision for pH measurements by contract laboratories (RMS standard deviation).

Parameter	Laboratory Duplicates (N = 127)	Field Duplicates (N = 125)
pH (equilibrated)	0.077	0.085
pH (alkalinity)	0.042	0.052
pH (acidity)	0.065	0.075

TABLE 3-3. Within-batch precision of laboratory duplicates.

Parameter[a]	Pairs with Mean > 0		Quantitation Limit (10 s_B)[b]	Pairs With Mean > 10 s_B	
	No. of Pairs	RMS RSD (%)		No. of Pairs	RMS RSD (%)
Calcium	123	0.89	0.15	123	0.89
Magnesium	121	0.63	0.039	121	0.63
Potassium	125	18	0.37	98	1.2
Sodium	123	13	0.20	119	0.97
Manganese	102	21	0.093	36	1.6
Iron	120	14	0.12	71	3.0
Aluminum (extractable)	123	13	0.039	45	18
Chloride	127	23	0.39	85	8.2
Sulfate	127	11	1.7	104	12
Nitrate	122	13	3.4	0	--
Silica	127	2.5	2.3	64	2.2
Fluoride (total)	127	2.5	0.034	120	2.5
DOC[c]	126	6.8	2.5	96	2.3
Mean > 5 mg/l				41	2.4
Mean < 5 mg/l				55	2.2
Ammonium	121	7.1	0.56	19	1.4
Acidity (µeq/l)	112	28	150	5	10.
Alkalinity (µeq/l)	116	30.	57	86	2.1
Conductivity (µS/cm)	125	11	9.0	122	11
DIC (equilibrated)	126	7.1	0.56	99	2.4
DIC (initial)	127	3.7	1.1	93	2.4
Phosphorus (total)	125	13	0.037	20	19
Aluminum (total)	126	19	0.28	9	5.4

[a] All parameters are measured in mg/l unless otherwise stated.
[b] s_B is standard deviation of measurements of blank samples.
[c] Precision goals for DOC are different above and below 5 mg/l.

TABLE 3-4. Within-batch precision of field duplicates.

	Pairs with Mean > 0			Pairs With Mean > 10 s_B	
Parameter[a]	No. of Pairs	RMS RSD (%)	Quantitation Limit (10 s_B)[b]	No. of Pairs	RMS RSD (%)
Calcium	125	2.3	0.15	125	2.3
Magnesium	125	2.3	0.039	125	2.3
Potassium	125	4.7	0.37	82	3.7
Sodium	125	4.2	0.20	121	4.3
Manganese	82	57	0.093	6	11
Iron	118	97	0.12	32	10.
Aluminum (extractable)	112	39	0.039	9	11
Chloride	123	15.	0.39	85	17
Sulfate	125	6.6	1.7	115	6.5
Nitrate	116	140	3.4	1	65
Silica	120	44	2.3	50	2.7
Fluoride (total)	125	8.2	0.034	62	9.0
DOC[c]	125	9.8	2.5	105	10.
Mean > 5 mg/l				59	12.
Mean < 5 mg/l				46	5.8
Ammonium	113	34	0.56	0	--
Acidity (µeq/l)	118	700	150	3	74
Alkalinity (µeq/l)	121	20.	57	90	10.
Conductivity (µS/cm)	125	1.9	9.0	125	1.9
DIC (equilibrated)	124	12	0.56	94	5.0
DIC (initial)	125	6.9	1.1	85	3.7
Phosphorus (total)	122	37	0.037	4	9.7
Aluminum (total)	125	35	0.28	1	24

[a] All parameters are measured in mg/l unless otherwise stated.
[b] s_B is standard deviation of measurements of blank samples.
[c] Precision goals for DOC are different above and below 5 mg/l.

TABLE 3-5. Very high RSDs in laboratory duplicate pairs with a mean measuement above the quantitation limit.

Parameter	Highest RSD (percent)	Batch	Next Highest RSD (percent)	Root Mean Square RSD Eliminating this Pair (percent)
Aluminum (extractable)	118	518	9.7	3.3
Chloride	73	105	7.1	2.1
Sulfate	117	317	5.9	1.3
Acidity	21	605	1.7	1.3
Conductivity	116	510	3.7	0.72
Phosphorus (total)	84	500	6.8	2.4

4 NATURAL AUDIT SAMPLES

INTRODUCTION

Large quantities of water were collected from Big Moose Lake and Lake Superior some months before the Eastern Lake Survey. Two-liter samples of this water were shipped daily to the field stations, where they were handled like the routine samples; the field stations prepared aliquots and shipped them to the contract laboratories with coded labels along with the day's routine samples.

Measurements of these natural audit samples give information about two aspects of the measuring process and consequently about the quality of the routine data. First, they are measurements by different laboratories of the same thing, provided the actual composition of the samples is constant. If the measurements by these laboratories differ systematically, we cannot tell which of two laboratories is right, if either, because we have no way of knowing exactly what is in the natural audit samples. We can, however, estimate the relative bias, i.e., the adjustment required to make measurements from the different laboratories comparable. Second, random variations in repeated measurements of the same thing are an indication of the precision of the measurements, again assuming the actual composition is constant.

METHOD

Measurement bias between laboratories, measurement precision, and changes in the samples over time are all related. All three are visible in Figure 4-1, which shows the measurements of initial pH from the acidity titration of samples from Big Moose Lake (type FN2) performed by EMSI and Versar. On the whole, in Figure 4-1 the E's are above the V's: there is an upward bias of the measurements by EMSI relative to those by Versar, or, equivalently, a downward bias by Versar relative to EMSI. There is an upward trend in the measurements over time: later ones are rather higher than earlier ones on average. There is also some scatter, or imprecision, in measurements by the same laboratory at about the same time.

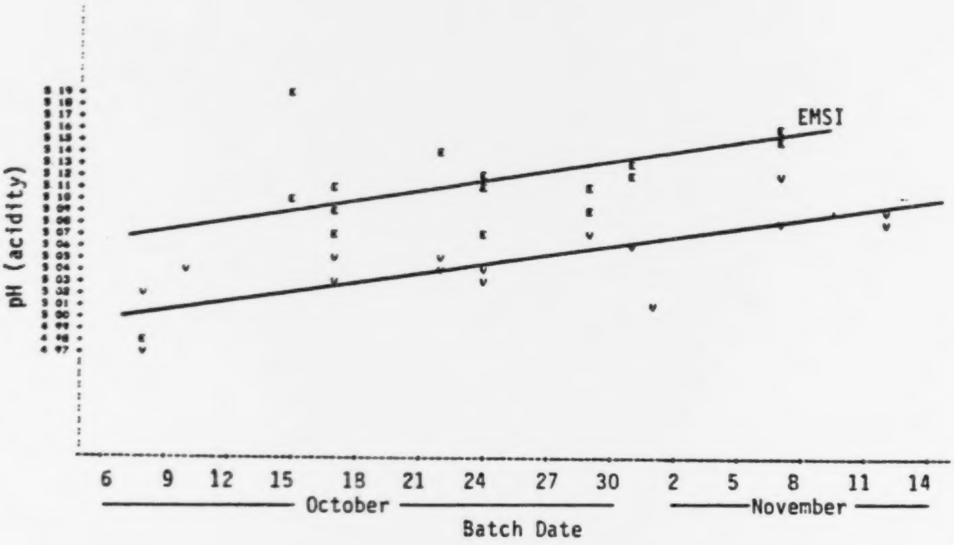

FIGURE 4-1. Interlaboratory bias and trend in pH of natural audits from Big Moose Lake (EMSI and Versar only).

The upward trend in measurements over time is somewhat hidden by the interlaboratory bias. The latest measurements are by Versar and so probably a little lower than if they had been by EMSI. The trend would have looked stronger if the latest measurements had been higher, and they probably would have been higher but for the bias. Indeed the trend in each of the laboratories separately is stronger than when they are combined.

Conversely, the increase in measured values over time hides some of the bias. Since the measurements by Versar are on average slightly later than those by EMSI, they are probably slightly higher than if they had been performed earlier. Thus, the bias shows up a little less if the averages of all measurements by EMSI and by Versar are compared than if measurements by the two laboratories around the same time are compared.

It seems reasonable to estimate bias and measurement trend simultaneously by the technique known as analysis of covariance. Separate but parallel least-squares lines are fit for the two laboratories. Bias is estimated by the vertical distance between the lines: this is the average difference between contemporaneous measurements. The trend is estimated by the common slope, which is the slope of the measurements corrected for bias.

Precision can be estimated two ways. If the estimates of bias and trend are assumed to be correct, measurements can be corrected for both. The precision of such corrected measurements is estimated by the standard deviation of the audit measurements around their respective least-squares lines. On the other hand, the estimated bias and trend are small compared to the residual scatter. It might, therefore, be just as well not to correct the measurements. In this case the precision is estimated simply by the standard deviation of the audit measurements.

The picture is much less neat when the other two laboratories are added (Figure 4-2). Versar's and EMSI's measurements are in October and early November, but USGS's are in December. The analysis of covariance extrapolates the linear trend from October and November into December. If that were true, the USGS measurements should be very high, unless they are biased. Accordingly, a very large negative bias is estimated for USGS's to account for their being about the same as Versar's on average.

There is no evidence in the data of a linear upward trend into December. On the other hand, there is no way to distinguish a change in the trend from a bias at USGS because there are no other measurements contemporaneous with USGS's. The best we can do is to estimate bias ignoring trend, by analysis of variance, as well as controlling for trend by analysis of covariance. The disparity of the estimates of bias for USGS by the two

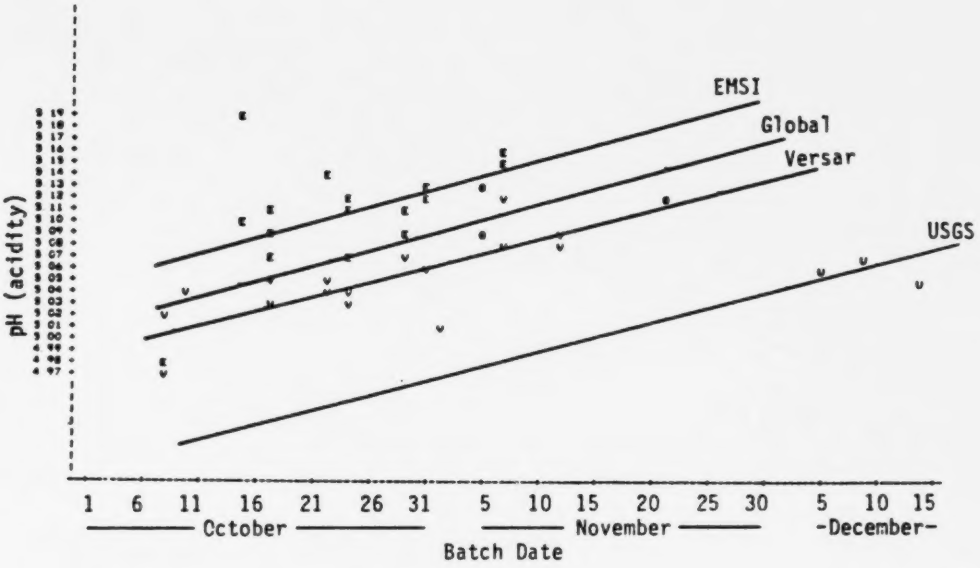

FIGURE 4-2. Interlaboratory bias and trend in pH of natural audits from Big Moose Lake (four laboratories).

methods is a warning of the uncertainty of these estimates. Incidentally, the analysis of variance provides a third estimate of precision--correcting for bias but ignoring trend.

RESULTS

Precision

Estimates of precision for parameters other than pH are shown in Table 4-1. Since precision for these parameters is believed to be roughly proportional to concentration, it is reported as a relative standard deviation (RSD), which is the appropriate standard deviation divided by the mean. (The standard deviation can be the ordinary standard deviation, ignoring bias and trend; within-laboratory standard deviation from the analysis of variance, correcting for bias; or residual standard deviation from the analysis of covariance, correcting for bias and trend.) For Lake Superior there are only seven samples, too few to estimate bias or trend; thus only the estimated precision ignoring bias and trend is reported. Table 4-1 also shows the means and the quantitation limit. If the concentration is below or near this limit, a high RSD is expected since large relative errors may occur at low concentrations. Iron, for example, is simply not found in determinable quantities in the natural audit samples. The estimates of precision for iron should therefore not be taken as representative of the precision with which iron is measured at higher concentrations.

On the whole, correcting for bias alone or for both bias and trend makes little difference in the estimates of precision. The biases and trends are small compared to the random variation even though they are sometimes large enough and systematic enough to be statistically significant.

For pH, since precision is more or less constant over the relevant range, there is no need for RSDs. (Anyway, absolute differences in pH already represent relative differences in hydrogen ion concentration.) Therefore the estimates of precision for pH are in pH units rather than percents. Also, there is no problem of quantitation limits for the pH measurements. The estimates of precision for pH are in Table 4-2.

Bias

The estimates of bias, both correcting for trend and ignoring trend, are shown in Tables 4-3 and 4-4. Like precision, bias might be supposed to be roughly proportional to concentration; accordingly, we show bias as a percentage of the mean. Again, pH measurements are an exception and are

TABLE 4-1. Overall precision estimated from natural audits.

	Big Moose Lake (N = 41)				Lake Superior (N = 7)		
	RSD(%)				RSD(%)		
Parameter*	Ignoring Bias and Trend	Correcting for Bias	Correcting for Bias and Trend	Mean	Ignoring Bias and Trend	Mean	Quantitation Limit
Calcium	9.2	6.5	6.4	1.9	5.5	13	0.15
Magnesium	2.7	1.9	1.9	0.35	3.6	2.8	0.039
Potassium	4.3	4.4	4.4	0.49	12	0.49	0.37
Sodium	5.1	4.7	4.4	0.67	6.4	1.3	0.20
Manganese	26	23	23	0.070	360	0.003	0.093
Iron	66	65	65	0.02	140	0.003	0.12
Aluminum (extractable)	34	32	32	0.18	86	0.002	0.039
Chloride	51	50.	50.	0.61	2.0	1.4	0.39
Sulfate	7.3	7.4	7.2	6.9	3.3	3.3	1.7
Nitrate	25	26	26	1.6	5.8	1.4	3.4
Silica	8.1	7.3	7.4	4.3	6.0	2.7	2.3
Fluoride (total)	4.1	3.9	3.9	0.077	5.1	0.035	0.034
DOC	9.3	8.7	8.8	3.3	9.7	1.4	2.5
Ammonium	54	50.	50.	0.059	130	0.007	0.56
Acidity (µeq/l)	40.	36	34	51	63	30.	150
Alkalinity (µeq/l)	260	246	249	2.4	2.3	850	57
Conductivity (µS/cm)	3.6	2.8	2.8	27	1.7	96	9.0
DIC (equilibrated)	60.	53	53	0.19	3.8	9.7	0.56
DIC (initial)	27	17	15	0.42	4.2	9.9	1.1
Phosphorus (total)	140	140	128	0.002	140	0.001	0.037
Aluminum (total)	28	22	21	0.31	120	0.021	0.28

* All parameters are measured in mg/l unless otherwide stated.

TABLE 4-2. Overall precision of pH measurements in natural audits.

	Big Moose Lake (N = 41)				Lake Superior (N = 7)	
		Precision				
Parameter	Mean	Ignoring Bias and Trend	Correcting for Bias	Correcting for Bias and Trend	Mean	Precision Ignoring Bias and Trend
pH (equilibrated)	5.18	0.27	0.27	0.28	8.23	0.08
pH (alkalinity)	5.07	0.04	0.04	0.03	7.76	0.12
pH (acidity)	5.08	0.05	0.04	0.03	7.79	0.11

TABLE 4-3. Relative interlaboratory bias (expressed as a percent of the mean) estimated from natural audits and controlling for measurement trend (estimate ± standard error of estimate).

	EMSI - Global	EMSI - USGS	EMSI - Versar	Global - USGS	Global - Versar	USGS - Versar
Calcium	0.6 ± 4.4	-32.0 ± 6.3	-1.1 ± 2.2	-32.6 ± 6.1	-1.8 ± 4.4	30.8 ± 6.3
Magnesium	0.1 ± 1.3	-5.7 ± 1.8	-3.8 ± 0.6	-5.8 ± 1.8	-3.9 ± 1.3	1.9 ± 1.8
Potassium	-0.2 ± 3.0	-0.1 ± 4.3	2.1 ± 1.5	0.1 ± 4.2	2.3 ± 3.0	2.2 ± 4.3
Sodium	0.7 ± 3.0	4.1 ± 4.3	3.2 ± 1.5	3.4 ± 4.2	2.4 ± 3.0	-0.9 ± 4.3
Manganese	-40.5 ± 15.5	22.0 ± 22.3	6.3 ± 7.7	62.6 ± 21.6	46.8 ± 15.4	-15.8 ± 22.1
Iron	47.6 ± 44.5	0.2 ± 64.0	12.5 ± 22.1	-47.3 ± 61.9	-35.1 ± 44.3	12.2 ± 63.6
Aluminum (extractable)	21.1 ± 21.5	-31.3 ± 31.0	-16.9 ± 10.7	-52.4 ± 30.0	-38.0 ± 21.4	14.4 ± 30.8
Chloride	14.8 ± 33.7	-3.6 ± 48.6	-30.2 ± 16.8	-18.4 ± 47.0	-45.0 ± 33.6	-26.6 ± 48.2
Sulfate	-0.5 ± 4.9	-13.7 ± 7.1	-1.5 ± 2.4	-13.2 ± 6.9	-1.0 ± 4.9	12.2 ± 7.0
Nitrate	-0.4 ± 17.4	-18.5 ± 25.1	5.1 ± 8.7	-18.1 ± 24.3	5.4 ± 17.4	23.6 ± 24.9
Silica	-12.9 ± 5.1	-0.7 ± 7.3	3.2 ± 2.5	12.2 ± 7.0	16.1 ± 5.0	3.9 ± 7.2
Fluoride (total)	-4.3 ± 2.7	-0.9 ± 3.9	-2.9 ± 1.3	3.4 ± 3.7	1.4 ± 2.7	-2.0 ± 3.8
DOC	-4.5 ± 6.0	-15.6 ± 8.6	2.5 ± 3.0	-11.1 ± 8.4	7.0 ± 6.0	18.1 ± 8.6
Ammonium	-51.9 ± 34.1	-30.1 ± 49.1	40.5 ± 16.9	21.8 ± 47.5	92.4 ± 34.0	70.7 ± 48.7
Acidity	77.9 ± 22.9	119.1 ± 33.0	4.7 ± 11.4	41.2 ± 31.9	-73.2 ± 22.9	-114.4 ± 32.8
Alkalinity	-27.8 ± 169.7	385.8 ± 244.4	146.4 ± 84.3	413.6 ± 236.4	174.2 ± 169.1	-239.4 ± 242.6
Conductivity	3.4 ± 1.9	-9.2 ± 2.8	0.5 ± 1.0	-12.6 ± 2.7	-2.9 ± 1.9	9.7 ± 2.8
DIC (equilibrated)	-102.5 ± 36.0	-15.1 ± 51.9	2.0 ± 17.9	87.4 ± 50.2	104.5 ± 35.9	17.1 ± 51.5
DIC (initial)	-79.8 ± 10.4	6.0 ± 15.0	-14.0 ± 5.2	85.7 ± 14.5	65.8 ± 10.4	-20.0 ± 14.9
Phosphorus (total)	107.6 ± 87.2	161.0 ± 125.7	-1.0 ± 43.3	53.4 ± 121.5	-108.6 ± 87.0	-162.0 ± 124.7
Aluminum (total)	47.7 ± 14.6	90.0 ± 21.1	23.6 ± 7.3	42.3 ± 20.4	-24.1 ± 14.6	-66.4 ± 20.9

TABLE 4-4. Relative interlaboratory bias (expressed as a percent of the mean) estimated from natural audits and ignoring measurement trend (estimate ± standard error estimate).

	EMSI - Global	EMSI - USGS	EMSI - Versar	Global - USGS	Global - Versar	USGS - Versar
Calcium	3.0 ± 4.1	-25.5 ± 4.1	-1.0 ± 2.2	-28.5 ± 5.3	-4.0 ± 4.1	24.5 ± 4.1
Magnesium	0.8 ± 1.2	-3.8 ± 1.2	-3.8 ± 0.6	-4.5 ± 1.6	-4.5 ± 1.2	-0.0 ± 1.2
Potassium	0.4 ± 2.7	1.4 ± 2.7	2.2 ± 1.5	1.1 ± 3.6	1.8 ± 2.7	0.7 ± 2.7
Sodium	-2.4 ± 2.9	-4.7 ± 2.9	3.0 ± 1.6	-2.2 ± 3.9	5.5 ± 3.0	7.7 ± 3.0
Manganese	-50.0 ± 14.4	-4.0 ± 14.4	5.9 ± 7.8	46.0 ± 18.9	55.8 ± 14.5	9.9 ± 14.5
Iron	66.3 ± 40.8	51.9 ± 40.8	13.3 ± 22.1	-14.4 ± 53.4	-53.0 ± 40.9	-38.6 ± 40.9
Aluminum (extractable)	34.4 ± 20.0	5.4 ± 20.0	-16.3 ± 10.9	-29.0 ± 26.2	-50.7 ± 20.1	-21.7 ± 20.1
Chloride	-3.0 ± 31.2	-52.9 ± 31.2	-30.9 ± 16.9	-49.9 ± 40.8	-27.9 ± 31.3	21.9 ± 31.3
Sulfate	2.6 ± 4.6	-5.4 ± 4.6	-1.4 ± 2.5	-7.9 ± 6.0	-3.9 ± 4.6	4.0 ± 4.6
Nitrate	10.4 ± 16.2	11.3 ± 16.2	5.5 ± 8.8	0.9 ± 21.3	-4.9 ± 16.3	-5.8 ± 16.3
Silica	-11.9 ± 4.6	2.0 ± 4.6	3.3 ± 2.5	13.9 ± 6.0	15.1 ± 4.6	1.2 ± 4.6
Fluoride (total)	-4.5 ± 2.4	-1.4 ± 2.4	-3.0 ± 1.3	3.0 ± 3.2	1.5 ± 2.4	-1.5 ± 2.4
DOC	-3.7 ± 5.4	-13.4 ± 5.4	2.5 ± 2.9	-9.7 ± 7.1	6.2 ± 5.4	15.9 ± 5.4
Ammonium	-42.1 ± 31.0	-3.2 ± 31.0	40.9 ± 16.8	39.0 ± 40.6	83.1 ± 31.1	44.1 ± 31.1
Acidity	55.8 ± 22.3	57.9 ± 22.3	3.8 ± 12.1	2.1 ± 29.2	-52.0 ± 22.4	-54.1 ± 22.4
Alkalinity	-50.7 ± 153.5	322.7 ± 153.7	145.4 ± 83.2	373.3 ± 200.9	196.1 ± 154.1	-177.2 ± 154.1
Conductivity	4.2 ± 1.8	-7.1 ± 1.8	0.5 ± 1.0	-11.2 ± 2.3	-3.7 ± 1.8	7.6 ± 1.8
DIC (equilibrated)	-113.5 ± 32.8	-45.4 ± 32.8	1.5 ± 17.8	68.1 ± 42.9	115.0 ± 32.9	46.9 ± 32.9
DIC (initial)	-68.2 ± 10.4	38.0 ± 10.4	-13.5 ± 5.6	106.2 ± 13.6	54.7 ± 10.4	-51.5 ± 10.4
Phosphorus (total)	6.9 ± 87.3	-117.3 ± 87.3	-5.3 ± 47.4	-124.2 ± 114.3	-12.2 ± 87.7	112.1 ± 87.7
Aluminum (total)	37.8 ± 13.7	62.7 ± 13.7	23.1 ± 7.4	24.9 ± 17.9	-14.6 ± 13.8	-39.5 ± 13.8

shown separately in Table 4-5. Each estimate of relative bias between two laboratories is accompanied by its standard error, a measure of the statistical uncertainty in the estimate. Again, we caution that the uncertainty for estimates involving USGS may be much greater because bias and trend cannot be distinguished in the data from this laboratory. The magnitude of this sort of uncertainty is suggested by the difference between corresponding estimates ignoring and controlling for trend.

There are three different standards against which the biases should be measured; the biases are on the whole rather small on all three scales. First, the biases are small compared to the precision of the individual measurements. This is why correcting for bias did not improve precision much. Correcting for bias improves the precision of initial dissolved inorganic carbon from 27 to 17 percent, the largest change among the parameters in this study but still only about a third. For most parameters the effect is much smaller. Thus, bias is small in the sense that it does not contribute much to the inaccuracy of individual measurements.

Second, bias is a small percentage of the average measured concentration in most cases. Most of the exceptions fall into three categories: (a) estimates involving USGS, which are not very reliable; (b) estimates for parameters for which precision is also relatively poor, e.g., chloride; and (c) estimates for parameters that are not present in the samples in amounts large enough to measure accurately, e.g., iron.

Finally, in many but not all cases the estimated bias is small compared to the standard error of the estimate. For example, the relative bias for calcium measurements by EMSI and Versar is about 1 percent, but this estimate is subject to an uncertainty of about 2 percent. In such cases the evidence that there is any bias at all is not statistically significant.

Trend

Table 4-6 shows the estimates of linear trends in the measurement of the parameters over time. Like the biases, the trends are small compared to (a) the precision of the measurements, (b) the measurements themselves, and (c) usually, but not always, the uncertainty in estimating them. Statistically significant trends (t-test, $p < .05$), all upward, are seen for sodium, acidity, initial dissolved inorganic carbon, total phosphorus, and initial pH from both acidity and alkalinity titrations.

TABLE 4-5a. Interlaboratory bias (expressed as pH units) estimated from natural audits: controlling for measurement trend (estimate ± standard error of estimate).

	EMSI - Global	EMSI - USGS	EMSI - Versar	Global - USGS	Global - Versar	USGS - Versar
pH (equilibrated)	0.1 ± 0.2	0.02 ± 0.3	0.1 ± 0.1	0.1 ± 0.3	0.0 ± 0.2	-0.1 ± 0.3
pH (alkalinity)	-0.02 ± 0.02	0.13 ± 0.03	0.02 ± 0.01	0.15 ± 0.03	0.04 ± 0.02	-0.11 ± 0.03
pH (acidity)	0.04 ± 0.02	0.16 ± 0.03	0.06 ± 0.01	0.12 ± 0.03	0.03 ± 0.02	-0.10 ± 0.03

TABLE 4-5b. Ignoring measurement trend.

	EMSI - Global	EMSI - USGS	EMSI - Versar	Global - USGS	Global - Versar	USGS - Versar
pH (equilibrated)	0.1 ± 0.2	0.2 ± 0.2	0.1 ± 0.1	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2
pH (alkalinity)	-0.05 ± 0.02	0.03 ± 0.02	0.02 ± 0.01	0.08 ± 0.03	0.08 ± 0.02	-0.01 ± 0.02
pH (acidity)	0.00 ± 0.02	0.05 ± 0.02	0.06 ± 0.01	0.05 ± 0.03	0.06 ± 0.02	0.01 ± 0.02

TABLE 4-6. Trends (per month) in measurements of natural audit samples (Big Moose Lake).

Parameter*	Estimated Trend	Standard Error of Estimate
Calcium	-0.08	0.06
Magnesium	-0.004	0.003
Potassium	0.00	0.01
Sodium	0.03	0.01
Manganese	0.012	0.008
Iron	-0.007	0.007
Aluminum (extractable)	-0.04	0.03
Chloride	0.20	0.15
Sulfate	-0.4	0.3
Nitrate	-0.3	0.2
Silica	-0.1	0.2
Fluoride (total)	0.000	0.002
DOC	0.0	0.1
Ammonium	-0.011	0.015
pH (equilibrated)	0.0	0.1
pH (alkalinity)	0.07	0.01
pH (acidity)	0.07	0.02
Acidity (μeq/l)	20.	9
Alkalinity (μeq/l)	1	3
Conductivity (μS/cm)	-0.4	0.4
DIC (equilibrated)	0.04	0.05
DIC (initial)	-0.09	0.03
Phosphorus (total)	0.003	0.001
Aluminum (total)	0.05	0.03

* All parameters measued in mg/l unless otherwise noted.

5 SYNTHETIC AUDIT SAMPLES

INTRODUCTION

Four kinds of synthetic audit samples were used in the Eastern Lakes Survey. All synthetic audits were mixed and diluted from stock solutions according to one of two recipes, one giving relatively high concentrations, the other low. "Field synthetic audits," like the natural audits, were sent daily in two-liter containers to the field stations, where they were processed into aliquots by the usual procedure. "Laboratory synthetic audits" arrived at the field station as aliquots; the field stations, without opening the aliquots, simply relabeled them and shipped them with the routine samples to the contract laboratories.

In addition to their use in quality control, the synthetic audits have three uses in quality assessment: estimation of precision and interlaboratory bias; comparison of measured with theoretical concentrations; and evaluation of performance of field stations by comparison of field and laboratory audits. Each of these three subjects is discussed in turn.

BIAS AND PRECISION

In principle, the synthetic audits, like the natural audits, can be used to estimate precision and interlaboratory bias. Differences in measurements of the same thing in the same laboratory at different times indicate how precise those measurements are. Systematic differences in measurements of the same thing between different laboratories indicate a relative bias between the laboratories. Unfortunately, there is ample evidence that the synthetic audit data are not repeated measurements of the same thing.

Figure 5-1 shows the concentrations of ammonium measured in laboratory high synthetic audit samples by three contract laboratories. With one exception (a measurement of about 1.9 mg/l by Versar on 18 October) the measurements on individual days form very tight groups, but the groups are spread far apart. That is, measurements on a given day are in close agreement both within and among laboratories, but on different days they

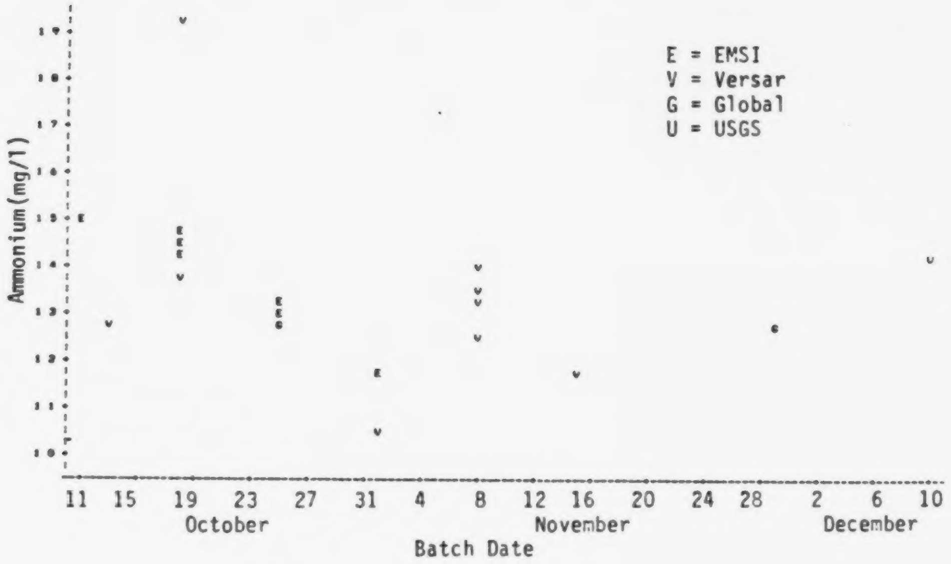

FIGURE 5-1. Concentration of ammonium measured in laboratory high synthetic audit samples.

are very different. Probably the concentrations were very different on different days, and imprecision in measurement and bias among laboratories were very small by comparison.

We would like to be able to quantify this comparison. An appropriate statistical technique is analysis of variance with fixed and random effects. Basically, differences between days are attributed to errors in preparation of the audit samples, and differences within days are attributed to errors in measurement. But we need to consider many variables, or effects, as they are called in statistics. There may be bias between laboratories. Measurements within a laboratory on the same day may be less variable than those on different days. There may be variation in preparation of the several samples on the same day, though less than across days. There may be systematic as well as random errors in preparation across time. With enough data all these effects could be estimated, but in this study there are not enough data. We did fit some random-effects models, but we consider the results wholly unreliable. The estimates are extremely sensitive both to single data points (like the exceptional 18 October ammonium concentration mentioned earlier) and to the statistical method of estimation chosen from several equally reasonable alternatives. With such large errors in preparation there is simply not enough information in the synthetic audits to estimate errors in measurement.

MEASURED VERSUS THEORETICAL CONCENTRATIONS

Comparing the concentration measured in the synthetic audit samples with the theoretical concentrations furnishes very useful confirmation that the system is measuring what it was meant to measure. Tables 5-1 and 5-2 show the theoretical values and the means of the measurements of field and laboratory, high and low synthetic audit samples (calcium and chloride are divided by lot because the theoretical concentrations changed between lots). For most parameters there is reasonable if not very close agreement between the measured and theoretical values.

The most notable exception is iron, which is essentially absent from the field audit samples but present in the laboratory audits. (Although there is no theoretical concentration, a similar difference is seen between field and laboratory audits for extractable aluminum; a smaller difference is seen for manganese). Apparently iron is removed by the processing in the field. Also, initial dissolved inorganic carbon is consistently above its theoretical value (Figure 5-2). However, some confusion is added by an apparent change in preparation around 23 October. This change is also

TABLE 5-1. Field and laboratory high synthetic audits.

Parameter*	Field (n = 36)		Laboratory (n = 21)		Theoretical
	Mean	Standard Deviation	Mean	Standard Deviation	
Calcium					
Lot 4 (n = 20, 14)	1.66	0.11	1.55	0.18	1.54
Lots 5, 6 (n = 16, 7)	1.95	0.16	1.96	0.10	2.39
Magnesium	2.37	0.09	2.36	0.08	2.43
Potassium	3.03	0.19	3.02	0.15	2.97
Sodium	11.84	1.03	11.87	1.04	12.41
Manganese	1.19	0.16	1.39	0.04	1.50
Iron	0.001	0.099	0.175	0.019	0.15
Aluminum (extractable)	0.037	0.027	0.161	0.030	--
Chloride					
Lot 4 (n = 20, 14)	3.66	1.45	3.39	0.24	2.72
Lots 5, 6 (n = 16, 7)	4.00	0.73	5.81	5.34	4.22
Sulfate	14.39	0.80	14.47	0.69	14.09
Nitrate	1.816	0.666	1.431	0.672	1.707
Silica	9.23	1.26	9.42	1.39	10.70
Fluoride (total)	0.445	0.042	0.435	0.012	0.452
DOC	10.01	1.96	10.25	1.68	10.0
Ammonium	1.256	0.162	1.342	0.176	1.25
pH (equilibrated)	7.72	0.54	7.87	0.15	--
pH (alkalinity)	7.08	0.25	7.05	0.26	--
pH (acidity)	7.12	0.27	7.11	0.25	--
Acidity (μeq/l)	73	56	85	68	--
Alkalinity (μeq/l)	477	82	486	95	--
Conductivity (μS/cm)	104.5	4.2	104.3	4.1	--
DIC (equilibrated)	4.72	1.28	4.79	1.31	--
DIC (initial)	5.94	1.98	5.94	1.90	3.10
Phosphorus	0.057	0.013	0.061	0.010	0.075
Aluminum (total)	0.199	0.059	0.195	0.067	0.19

* Measured in mg/l unless other noted.

TABLE 5-2. Field and laboratory low synthetic audits.

	Field (n = 36)		Laboratory (n = 21)		
	Mean	Standard Deviation	Mean	Standard Deviation	Theoretical
Calcium					
Lot 4 (n = 20, 20)	0.144	0.027	0.137	0.015	0.13
Lots 5, 6 (n = 23, 23)	0.169	0.012	0.161	0.014	0.19
Magnesium	0.424	0.031	0.426	0.019	0.45
Potassium	0.231	0.043	0.225	0.023	0.20
Sodium	2.71	0.14	2.69	0.25	2.79
Manganese	0.091	0.009	0.092	0.014	0.10
Iron	0.001	0.012	0.070	0.016	0.06
Aluminum (extractable)	0.005	0.004	0.018	0.006	--
Chloride					
Lot 4 (n = 20, 20)	0.329	0.234	0.300	0.042	0.22
Lots 5, 6 (n = 23, 23)	0.365	0.081	0.347	0.109	0.34
Sulfate	2.27	0.23	2.28	0.10	2.28
Nitrate	0.547	0.362	0.471	0.172	0.466
Silica	1.00	0.31	1.02	0.20	1.07
Fluoride (total)	0.042	0.009	0.040	0.002	0.042
DOC	0.982	0.476	1.190	0.724	1.0
Ammonium	0.158	0.043	0.186	0.041	0.17
pH (equilibrated)	7.34	0.14	7.29	0.13	--
pH (alkalinity)	6.87	0.11	6.86	0.12	--
pH (acidity)	6.96	0.19	6.93	0.15	--
Acidity (μeq/l)	16.3	23.3	16.1	27.3	--
Alkalinity (μeq/l)	112	8.3	110	10.3	--
Conductivity (μS/cm)	19.0	1.3	18.7	1.2	--
DIC (equilibrated)	1.35	0.12	1.35	0.15	--
DIC (initial)	1.65	0.21	1.65	0.24	0.96
Phosphorus (total)	0.021	0.006	0.022	0.009	0.027
Aluminum (total)	0.023	0.005	0.031	0.028	0.02

* Measured in mg/l unless otherwise noted.

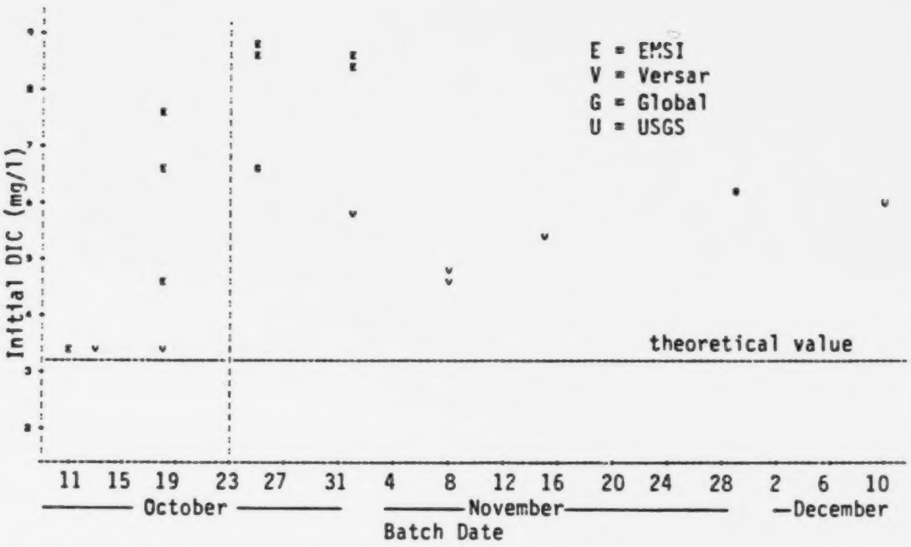

FIGURE 5-2. Concentration of dissolved inorganic carbon (initial) measured in laboratory high audit samples. Measurements before and after 23 October (vertical line) seem to be different.

noticed in several other parameters, especially sodium, silica (Figure 5-3), acidity, alkalinity, and pH, and may have been caused by a change in the concentration of the stock solution of sodium silicate.

We do not think any detailed statistical analysis of the differences between measured and theoretical concentrations is called for. The likeliest reason for any difference is not a problem in processing or analysis but rather that the theoretical concentrations are not what was actually in the samples.

FIELD VERSUS LABORATORY AUDITS

It was hoped that by comparing the variability of the field audits, which were processed by field stations, with that of the laboratory audits, which were not, one could distinguish the amount of variability introduced at the field stations from the imprecision of the analytical laboratories. As it happens, both of these sources of variability are swamped by variability in the preparation of synthetic audit samples. The standard deviations of measurements of the four types of synthetic audit samples (field and laboratory, high and low) are in Tables 5-1 and 5-2. On the whole the field audits are not any more variable than the laboratory audits. That is, preparation of the aliquots in the field introduces no more variability than preparation in the laboratory. Again, finer analysis is made impossible by the magnitude of the errors in preparation of synthetic audit samples.

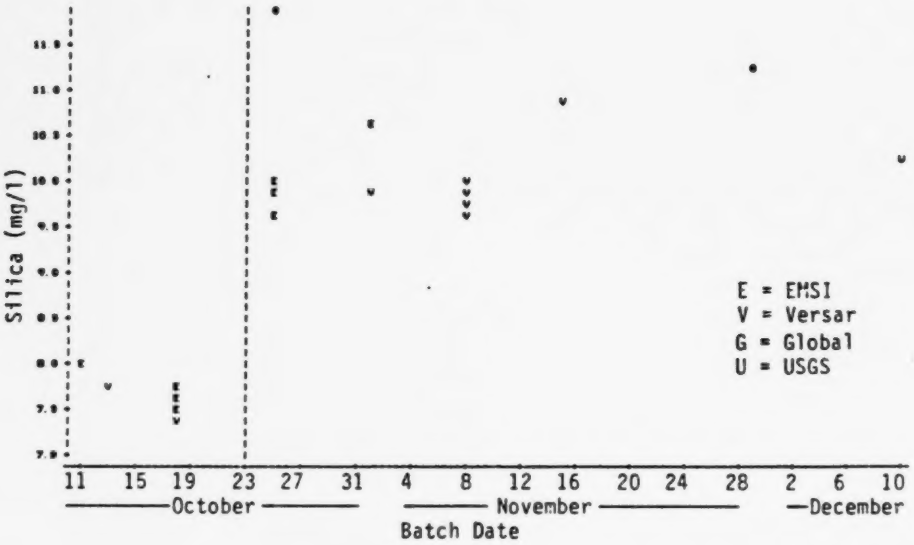

FIGURE 5-3. Concentration of silica measured in laboratory high synthetic audit samples. Measurements before and after 23 October (vertical line) seem to be different.

6 CONCLUSIONS AND RECOMMENDATIONS

WHAT THE QA DATA SHOW

One of the purposes of the QA data was to allow us to estimate the imprecision of routine lake sample measurements. In this report we have provided many estimates of various kinds of precision. In this section we relate all these estimates. Table 6-1 shows our estimates of within-batch laboratory precision, within-batch precision (including errors made both at the field stations and at the analytical laboratories), and overall precision. The estimates of precision are for measurements above the quantitation limit for each parameter, as we know that there are large relative errors below the quantitation limits.

The findings of our analysis may be illustrated by considering together the information given by all the quality assurance data about one parameter. We use calcium as the example. The estimate of measurement precision from laboratory duplicate pairs for calcium is 0.89 percent. Thus, the reproducibility of determinations of calcium within any single laboratory and single batch is excellent. When precision is estimated from field duplicate pairs, the estimate rises to 2.3 percent. So, when the entire system of collection, field processing, and laboratory analysis is considered (and when the contract laboratory is blind to the duplicates) reproducibility is much less but still very good. This reproducibility is still for measurements within the same laboratory and within the same batch. These are likely to be done by a single analyst, possibly off a single calibration, certainly on a single day, and so under broadly similar laboratory conditions.

Information about variation from day to day and from laboratory to laboratory comes from the natural audits. Within the same laboratory the estimated precision for the determination of calcium in Big Moose Lake samples is 6.5 percent. The measurements by the USGS laboratory are some 25 percent higher than the others, either because of bias or because of a change in the samples over time; consequently if all Big Moose Lake measurements are lumped together without regard to laboratory or date, the estimate of precision rises to 9.2 percent.

TABLE 6-1. Summary of estimates of precision (percent RSD, except for pH, which is expressed as SD in pH units).

	Natural Audits				
	Big Moose Lake		Lake Superior		
Parameter*	Correcting for Bias and Trend	Ignoring Bias and Trend	Ignoring Bias and Trend	Field Duplicates	Laboratory Duplicates
Calcium	6.4	9.2	5.5	2.3	0.89
Magnesium	1.9	2.7	3.6	2.3	0.63
Potassium	4.4	4.3	12	3.7	1.2
Sodium	4.4	5.1	6.4	4.3	0.97
Manganese	23	26	360	11	1.6
Iron	65	66	140	10.	3.0
Aluminum (extractable)	32	34	86	11	3.3
Chloride	50.	51	2.0	23	2.1
Sulfate	7.2	7.3	3.3	6.5	1.3
Nitrate	26	25	5.8	65	--
Silica	7.4	8.1	6.0	2.7	2.2
Floride (total)	3.9	4.1	5.1	9.0	2.5
DOC	8.8	9.3	9.7	10.	2.3
Ammonium	50.	54	130	--	1.4
Acidity	34	40.	63	74	1.3
Alkalinity	249	260	2.3	10.	2.1
Conductivity	2.8	3.6	1.7	1.9	0.72
DIC (equilibrated)	53	60.	3.8	5.0	2.4
DIC (initial)	15	27	4.2	3.7	2.4
Phosphorus (total)	128	140	140	9.7	2.4
Aluminum (total)	21	28	120	24	5.4
pH (equilibrated)	0.28	0.27	0.08	0.085	0.077
pH (alkalinity)	0.03	0.04	0.12	0.052	0.042
pH (acidity)	0.03	0.05	0.11	0.075	0.065

The rise from 0.89 to 2.3 to 6.5 to 9.2 percent as we move from the laboratory duplicates through the field duplicates to the natural audits is not surprising, and it demonstrates the importance of the quality assurance program. As it happened, the imprecision of a perfectly calibrated instrument under constant conditions made only a small contribution to overall uncertainty, compared to errors in calibration and variation over time in conditions or procedures in the laboratory and in the field. These other effects can only be judged by audits treated as much as possible like routine samples under field conditions. The blind field natural audits serve this purpose well. The estimates of precision from field natural audits are therefore probably the best indicators of uncertainty in the routine samples.

Along with calcium, the Big Moose Lake natural audits probably give reasonable estimates of overall precision in routine samples for magnesium, potassium, sodium, aluminum (extractable and total), chloride, sulfate, silica, fluoride, dissolved organic carbon, and all three measurements of pH by contract laboratories. The levels of other parameters in Big Moose Lake samples are below the quantitation limit, and the relative standard deviations at such low concentrations should not be considered representative. These parameters fall into three classes.

> Dissolved inorganic carbon (equilibrated and initial). There is quantifiable DIC in natural audit samples from Lake Superior. The RSD for these samples can be used as an estimate of overall precision in place of that for Big Moose Lake.
>
> Alkalinity. The alkalinity of samples from Lake Superior is well above the quantitation limit; indeed, at 850 µeq/l it is probably much higher than that of most lakes in the survey. The precision of Lake Superior measurements is therefore not representative of routine measurements. We therefore have no good estimate of overall precision for alkalinity. The closest we can come is the within-batch estimate of 10 percent from field duplicates, recognizing that within-batch calculations usually underestimate overall imprecision. On the other hand, the low synthetic audits, in spite of preparation error, also have RSDs around 10 percent, so that overall imprecision cannot be much higher. The figure of 10 percent is therefore a reasonable estimate of precision of measurements of alkalinity in routine samples.
>
> Nitrate, ammonium, acidity, phosphorus, iron, and manganese. The levels of these parameters in the natural audits are below the quantitation limits. So are the levels in almost all the lakes for which there are field or laboratory duplicates, and so presumably in almost all the routine samples. Thus these things were not measured

very precisely simply because there was not enough of them to measure. One could say that the lakes contained no measurable levels of these parameters, or that the system was insufficiently sensitive to measure what was in the lakes; the matter will be judged according to the quantitation limits.

SYNTHETIC AUDITS

The synthetic audit samples turned out not to be useful for estimating errors in measurement because these were much smaller than errors in preparation. In retrospect this is not surprising: it is hard to prepare something more accurately than one can measure it.

The synthetic audits, however, are the only samples that furnish one important kind of data, but not enough of them--measurements of split samples by different laboratories. Such measurements are very useful in estimating interlaboratory bias. For most parameters the stability of the natural audits is sufficient for this purpose, but it would be preferable to be able to compare measurements on the same day. Also, the natural audits are field audits and so include effects of processing by field stations, while laboratory synthetic audits could give information about bias between laboratories without involving field station effects.

We recommend that in the future synthetic audits always be treated as split samples. Daily lots should be prepared and divided into aliquots, and the aliquots should be assigned to different contract laboratories at random. The QA data base should identify the daily lot for each sample so that comparisons between laboratories can be made using data from the same lot. Variation among lots is then of little importance. Indeed it might even be desirable to vary the composition of samples between lots, both to prevent recognition of blind audit samples and to see precision and accuracy at various concentrations.

DETECTION LIMITS

To calculate detection limits from measurements of blank samples, we had to make certain unverifiable assumptions about the response of the measuring system at low concentrations. In particular, we assumed that the calibration of the system was linear (with slope 1) although the intercept need not be zero. Thus, some background might be added to samples in processing, but the amount of background should be independent of the concentration.

We believe that if detection limits are important, they should be determined empirically. That is, audit samples with a concentration near the putative detection limit for an analyte ought to be measured, and it should be seen whether the analyte is reliably detected or not. Decision limits, on the other hand, can be straightforwardly defined and accurately estimated from blank data alone.

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APPENDIX B

INSTRUMENTAL DETECTION LIMITS, SYSTEM DETECTION LIMITS, AND SYSTEM DECISION LIMITS BY LABORATORY, EASTERN LAKE SURVEY - PHASE I

Values were reported by the contract analytical laboratories or were estimated from field blank data and calibration blank data.

TABLE B-1.

	Reported Instrumental Detection Limit[a]			
Parameter	EMSI	Global	USGS	Versar
Al, total extractable, mg L^{-1}	0.002	0.002	0.003	0.003
Al, total, mg L^{-1}	0.002	0.002	0.002	0.004
Ca, mg L^{-1}	0.01	0.00	0.00	0.01
Cl^-, mg L^{-1}	0.00	0.00	0.00	0.01
Conductance, µS cm^{-1}	-0.4	-0.2	0.5	0.5
DIC, air-equilibrated, mg L^{-1}	0.02	0.04	0.03	0.003
DOC, mg L^{-1}	0.1	0.1	0.1	0.1
F^-, total dissolved, mg L^{-1}	0.003	0.001	0.002	0.002
Fe, mg L^{-1}	0.03	0.02	0.01	0.01
K, mg L^{-1}	0.00	0.00	0.01	0.01
Mg, mg L^{-1}	0.00	0.00	0.00	0.00
Mn, mg L^{-1}	0.01	0.01	0.00	0.00
Na, mg L^{-1}	0.00	0.00	0.00	0.00
NH_4^+, mg L^{-1}	0.01	0.00	0.01	0.01
NO_3^-, mg L^{-1}[b]	0.006	0.003	0.006	0.006
P, total, mg L^{-1}	0.001	0.001	0.001	0.001
SiO_2, mg L^{-1}	0.03	0.02	0.02	0.02
SO_4^{2-}, mg L^{-1}	0.01	0.01	0.03	0.03

[a] The arithmetic mean of the weekly reported instrumental detection limits (3 times the standard deviation of 10 nonconsecutive replicate laboratory calibration blank or reagent blank analyses (see Drousé et al. 1986).

[b] All batches (aliquots 3 and 5).

TABLE B-2.

	Estimated Instrumental Detection Limit[a]			
Parameter	EMSI	Global	USGS	Versar
Al, total extractable, mg L^{-1}	0.004	0.004	0.004	0.008
Al, total, mg L^{-1}	0.006	0.006	0.008	0.008
Ca, mg L^{-1}	0.00	0.02	0.00	0.00
Cl^-, mg L^{-1}	0.01	0.02	0.07	0.05
Conductance, µS cm^{-1}	0.6	0.0	0.5	0.5
DIC, air-equilibrated, mg L^{-1}	0.10	0.20	0.25	0.06
DOC, mg L^{-1}	0.2	0.0	0.6	0.2
F^-, total dissolved, mg L^{-1}	0.006	0.002	0.002	0.010
Fe, mg L^{-1}	0.02	0.02	0.01	0.00
K, mg L^{-1}	0.00	0.02	0.00	0.01
Mg, mg L^{-1}	0.00	0.00	0.00	0.00
Mn, mg L^{-1}	0.02	0.00	0.00	0.00
Na, mg L^{-1}	0.00	0.02	0.00	0.00
NH_4^+, mg L^{-1}	0.02	0.00	0.01	0.06
NO_3^-, mg L^{-1}[b]	0.038	0.048	0.000	0.061
P, total, mg L^{-1}	0.003	0.004	0.000	0.004
SiO_2, mg L^{-1}	0.03	0.02	--	0.16
SO_4^{2-}, mg L^{-1}	0.08	0.00	0.17	0.08

[a] Estimated instrumental detection limit = $2(P_{95} - P_{50})$ where P_{95} = 95th percentile, and P_{50} = 50th percentile, of laboratory calibration blank or reagent blank analyses.

[b] All batches (aliquots 3 and 5).

TABLE B-3.

	System Detection Limit[a]			
Parameter	EMSI	Global	USGS	Versar
Al, total extractable, mg L^{-1}	0.011	0.00	0.004	0.006
Al, total, mg L^{-1}	0.59	0.088	0.708	0.036
ANC, μeq L^{-1}	12	6.0	3.4	6.2
Ca, mg L^{-1}	0.08	0.10	0.02	0.06
Cl$^-$, mg L^{-1}	0.24	0.04	0.06	1.4
Conductance, μS cm^{-1}	1.8	1.0	1.0	0.8
DIC, air-equilibrated, mg L^{-1}	0.20	0.34	0.12	0.16
DIC, initial, mg L^{-1}	0.34	0.84	0.08	0.28
DOC, mg L^{-1}	0.6	1.0	0.6	0.4
F$^-$, total dissolved, mg L^{-1}	0.072	0.060	0.002	0.000
Fe, mg L^{-1}	0.02	0.00	0.00	0.00
K, mg L^{-1}	0.04	0.06	0.02	0.02
Mg, mg L^{-1}	0.00	0.02	0.02	0.00
Mn, mg L^{-1}	0.02	0.14	0.00	0.00
Na, mg L^{-1}	0.20	0.02	0.04	0.20
NH$_4^+$, mg L^{-1}	0.46	0.10	0.05	0.08
NO$_3^-$, mg L^{-1}[b]	0.096	0.082	0.048	0.270
NO$_3^-$, mg L^{-1}[c]	0.049	0.091	0.048	0.045
NO$_3^-$, mg L^{-1}[d]	0.118	0.066	--	0.341
P, total, mg L^{-1}	0.018	0.022	0.002	0.010
SiO$_2$, mg L^{-1}	0.14	0.34	0.02	0.40
SO$_4^{2-}$, mg L^{-1}	0.14	0.06	0.10	0.10

[a] System detection limit = 2(P_{95} - P_{50}), where P_{95} = 95th percentile, and P_{50} = 50th percentile, of field blank measurements.

[b] All batches (aliquots 3 and 5).

[c] Aliquot 3 after filtration protocol change.

[d] Aliquot 5.

TABLE B-4.

	System Decision Limit[a]			
Parameter	EMSI	Global	USGS	Versar
Al, total extractable, mg L^{-1}	0.008	0.004	-0.002	0.004
Al, total, mg L^{-1}	0.030	0.045	0.365	0.023
ANC, µeq L^{-1}	10.7	3.9	-8.9	3.1
Ca, mg L^{-1}	0.04	0.05	0.01	0.03
Cl^-, mg L^{-1}	0.13	0.02	0.04	0.10
Conductance, µS cm^{-1}	0.6	0.6	1.4	1.4
DIC, air equilibrated, mg L^{-1}	0.28	0.33	0.24	0.26
DIC, initial, mg L^{-1}	0.46	0.69	0.27	0.30
DOC, mg L^{-1}	0.5	0.6	0.5	0.4
F^-, total dissolved, mg L^{-1}	0.038	0.020	0.001	0.000
Fe, mg L^{-1}	0.01	0.00	0.00	0.00
K, mg L^{-1}	0.02	0.03	0.01	0.01
Mg, mg L^{-1}	0.00	0.01	0.01	0.00
Mn, mg L^{-1}	0.01	0.07	0.00	0.00
Na, mg L^{-1}	0.10	0.01	0.00	0.10
NH_4^+, mg L^{-1}	0.24	0.05	0.02	0.04
NO_3^-, mg L^{-1}[b]	0.056	0.041	0.024	0.131
NO_3^-, mg L^{-1}[c]	0.019	0.046	0.024	0.029
NO_3^-, mg L^{-1}[d]	0.068	0.033	--	0.167
P, total, mg L^{-1}	0.010	0.014	0.001	0.005
SiO_2, mg L^{-1}	0.08	0.17	0.01	0.15
SO_4^{2-}, mg L^{-1}	0.10	0.04	0.10	0.08

[a] System decision limit = P_{95}, where P_{95} = 95th percentile of field blank measurements.

[b] All batches (aliquots 3 and 5).

[c] Aliquot 3 after filtration protocol change.

[d] Aliquot 5.

APPENDIX C

OVERALL WITHIN-BATCH PRECISION BY LABORATORY FOR 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

Values were estimated from field duplicate and field blank data.

TABLE C-1. EMSI OVERALL WITHIN-BATCH PRECISION

	Pairs with Mean > 0		Pairs with Mean > 10s_B		Quantitation Limit	
Parameter	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	10s_B
Al, total extractable, mg L^{-1}						
all values	47	47	1	24	99	0.046
$\bar{x}$ <= 0.010	26	61	0	--		
x > 0.010	21	16	1	24		
Al, total, mg L^{-1}						
all values	51	39	3	36	99	0.187
$\bar{x}$ <= 0.010	0	--	0	--		
x > 0.010	51	39	3	36		
ANC, μeq L^{-1}	50	19	47	10	99	29.1
Ca, mg L^{-1}	51	2.6	51	2.6	99	0.13
Cl$^-$, mg L^{-1}	51	21	37	24	99	0.45
Conductance, μS cm^{-1}	51	1.8	51	1.8	99	5.9
DIC, mg L^{-1}						
air-equilibrated	51	3.9	44	2.2	99	0.52
initial	51	7.6	44	5.3	99	0.91
DOC, mg L^{-1}						
all values	51	14	40	15	99	2.7
$\bar{x}$ <= 5	29	8.0	18	6.5		
$\bar{x}$ > 5	22	20	22	20		
Fe, mg L^{-1}	49	141	4	14	99	0.18
F$^-$, total dissolved, mg L^{-1}	51	9.4	34	10	99	0.029
K, mg L^{-1}	51	6.5	51	6.5	99	0.10
Mg, mg L^{-1}	51	3.3	51	3.3	99	0.03
Mn, mg L^{-1}	46	69	4	13	99	0.06
Na, mg L^{-1}	51	1.9	49	1.9	99	0.28
NH$_4^+$, mg L^{-1}	51	18	0	--	97	0.80
NO$_3^-$, mg L^{-1}						
all batches	50	308	7	0.85	98	0.182
aliquot 3	12	6.1	4	1.7	21	0.009
aliquot 5	38	354	5	0.83	77	0.184
pH						
air-equilibrated	51	0.07	--	--	--	--
initial ANC	51	0.04	--	--	--	--
initial BNC	50	0.06	--	--	--	--
P, total, mg L^{-1}						
all values	48	40	0	--	99	0.005
$\bar{x}$ <= 0.010	33	45	0	--		
$\bar{x}$ > 0.010	15	27	0	--		
SiO$_2$, mg L^{-1}	51	20	42	20	99	0.04
SO$_4^{2-}$, mg L^{-1}	51	2.9	51	2.9	99	0.31

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE C-2. GLOBAL OVERALL WITHIN-BATCH PRECISION

	Pairs with Mean > 0		Pairs with Mean > 10s_B		Quantitation Limit	
Parameter	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	10s_B
Al, total extractable, mg L^{-1}						
all values	17	36	2	9.8	31	0.016
$\bar{x}$ <= 0.010	15	38	0	--		
x > 0.010	2	9.8	2	9.8		
Al, total, mg L^{-1}						
all values	17	21	5	23	30	0.128
$\bar{x}$ <= 0.010	3	30	0	--		
x > 0.010	14	19	5	23		
ANC, μeq L^{-1}	16	3.1	14	1.5	31	47.9
Ca, mg L^{-1}	17	4.1	17	4.1	31	0.20
Cl^-, mg L^{-1}	17	4.4	17	4.4	31	0.08
Conductance, μS cm^{-1}	17	4.1	17	4.1	31	2.6
DIC, mg L^{-1}						
air-equilibrated	16	11	14	11	31	0.97
initial	17	6.7	12	3.7	31	1.64
DOC, mg L^{-1}						
all values	17	5.9	12	5.4	31	1.9
$\bar{x}$ <= 5	9	7.8	4	8.6		
$\bar{x}$ > 5	8	2.6	8	2.6		
Fe, mg L^{-1}	16	21	4	16	31	0.13
F^-, total dissolved, mg L^{-1}	17	3.4	17	3.4	31	0.007
K, mg L^{-1}	17	2.0	17	2.0	31	0.09
Mg, mg L^{-1}	17	2.0	17	2.0	31	0.05
Mn, mg L^{-1}	11	46	0	--	31	0.23
Na, mg L^{-1}	17	3.0	17	3.0	31	0.06
NH_4^+, mg L^{-1}	17	21	0	--	31	0.15
NO_3^-, mg L^{-1}						
all batches	15	38	7	2.6	31	0.114
aliquot 3	10	27	3	2.0	23	0.114
aliquot 5	5	53	4	3.0	8	0.119
pH						
air-equilibrated	17	0.03	--	--	--	--
initial ANC	17	0.06	--	--	--	--
initial BNC	17	0.07	--	--	--	--
P, total, mg L^{-1}						
all values	17	44	0	--	31	0.044
$\bar{x}$ <= 0.010	10	38	0	--		
$\bar{x}$ > 0.010	7	51	0	--		
SiO_2, mg L^{-1}	17	3.7	16	3.8	31	0.54
SO_4^{2-}, mg L^{-1}	17	1.3	17	1.3	31	0.12

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE C-3. USGS OVERALL WITHIN-BATCH PRECISION

Parameter	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
all values	6	6.6	0	--	18	0.024
$\bar{x} <= 0.010$	1	0.00	0	--		
$x > 0.010$	5	7.2	0	--		
Al, total, mg L^{-1}						
all values	10	34	0	--	18	0.850
$\bar{x} <= 0.010$	0	--	0	--		
$x > 0.010$	10	34	0	--		
ANC, μeq L^{-1}	8	28	6	1.9	18	17.3
Ca, mg L^{-1}	10	0.47	10	0.47	18	0.03
Cl^-, mg L^{-1}	10	2.3	10	2.3	18	0.10
Conductance, μS cm^{-1}	10	0.65	10	0.65	18	1.9
DIC, mg L^{-1}						
air-equilibrated	10	10	8	6.9	18	0.38
initial	10	11	9	9.6	18	0.34
DOC, mg L^{-1}						
all values	10	3.7	9	3.9	18	1.1
$\bar{x} <= 5$	5	3.4	4	3.8		
$\bar{x} > 5$	5	4.0	5	4.0		
Fe, mg L^{-1}	9	67	6	7.1	18	0.00
F^-, total dissolved, mg L^{-1}	10	12	10	12	18	0.005
K, mg L^{-1}	10	1.4	10	1.4	18	0.03
Mg, mg L^{-1}	10	0.49	10	0.49	18	0.03
Mn, mg L^{-1}	7	58	2	18	18	0.01
Na, mg L^{-1}	10	1.0	10	1.0	18	0.02
NH_4^+, mg L^{-1}	10	23	2	3.2	18	0.05
NO_3^-, mg L^{-1}						
all batches	9	68	3	6.6	18	0.060
aliquot 3	9	68	3	6.6	18	0.060
aliquot 5	0	--	0	--	0	--
pH						
air-equilibrated	10	0.06	--	--	--	--
initial ANC	10	0.10	--	--	--	--
initial BNC	9	0.18	--	--	--	--
P, total, mg L^{-1}						
all values	10	18	9	19	18	0.004
$\bar{x} <= 0.010$	6	22	5	24		
$\bar{x} > 0.010$	4	11	4	11		
SiO_2, mg L^{-1}	10	3.7	8	2.3	18	0.14
SO_4^{2-}, mg L^{-1}	10	5.3	10	5.3	18	0.38

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE C-4. VERSAR OVERALL WITHIN-BATCH PRECISION

	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
Parameter	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
all values	43	52	10	37	97	0.020
$\bar{x}$ <= 0.010	27	62	0	--		
x > 0.010	16	29	10	37		
Al, total, mg L^{-1}						
all values	47	35	10	27	97	0.098
$\bar{x}$ <= 0.010	6	64	--	--		
x > 0.010	41	29	10	27		
ANC, μeq L^{-1}	47	21	32	13	97	43.9
Ca, mg L^{-1}	47	0.71	47	0.71	97	0.16
Cl^-, mg L^{-1}	47	24	28	30	97	0.37
Conductance, μS cm^{-1}	47	0.43	47	0.43	97	8.4
DIC, mg L^{-1}						
air-equilibrated	47	17	34	6.5	97	0.43
initial	47	4.8	45	4.7	97	0.56
DOC, mg L^{-1}						
all values	47	4.5	45	4.5	97	2.7
$\bar{x}$ <= 5	23	4.6	21	4.8		
$\bar{x}$ > 5	24	4.3	24	4.3		
Fe, mg L^{-1}	44	45	32	13	97	0.02
F^-, total dissolved, mg L^{-1}	47	6.6	14	3.2	97	0.041
K, mg L^{-1}	47	3.3	19	3.9	97	0.58
Mg, mg L^{-1}	47	0.75	47	0.75	97	0.04
Mn, mg L^{-1}	18	11	18	11	97	0.00
Na, mg L^{-1}	47	6.4	45	6.4	97	0.12
NH_4^+, mg L^{-1}	35	53	1	7.6	97	0.31
NO_3^-, mg L^{-1}						
all batches	39	667	0	--	97	1.406
aliquot 3	14	377	2	94	37	0.231
aliquot 5	25	780	0	--	60	1.765
pH						
air-equilibrated	47	0.11	--	--	--	--
initial ANC	47	0.05	--	--	--	--
initial BNC	47	0.05	--	--	--	--
P, total, mg L^{-1}						
all values	47	34	5	40	97	0.022
$\bar{x}$ <= 0.010	8	59	0	--		
$\bar{x}$ > 0.010	39	26	5	40		
SiO_2, mg L^{-1}	42	71	12	1.9	97	3.67
SO_4^{2-}, mg L^{-1}	47	9.9	28	11	97	2.64

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

APPENDIX D

ANALYTICAL WITHIN-BATCH PRECISION BY LABORATORY FOR 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

Values were estimated from contract analytical laboratory duplicate and calibration blank data.

TABLE D-1. EMSI ANALYTICAL WITHIN-BATCH PRECISION

	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
Parameter	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
all values	49	3.2	43	3.2	49	0.010
$\bar{x}$ <= 0.010	6	3.3	0	--		
x > 0.010	43	3.2	43	3.2		
Al, total, mg L^{-1}						
all values	49	17	48	17	49	0.011
$\bar{x}$ <= 0.010	1	7.6	0	--		
$\bar{x}$ > 0.010	48	17	48	17		
ANC, μeq L^{-1}	47	14	--	--	--	--
Ca, mg L^{-1}	49	1.1	49	1.1	49	0.03
Cl^-, mg L^{-1}	49	10	49	10	49	0.03
Conductance, μS cm^{-1}	49	0.81	49	0.81	49	2.4
DIC, mg L^{-1}						
air-equilibrated	49	3.5	27	1.7	48	0.73
initial	49	3.7	43	3.3	48	0.58
DOC, mg L^{-1}						
all values	49	1.6	49	1.6	49	0.4
$\bar{x}$ <= 5	25	1.7	25	1.7		
$\bar{x}$ > 5	24	1.4	24	1.4		
Fe, mg L^{-1}	47	8.5	36	4.1	49	0.07
F^-, total dissolved, mg L^{-1}	49	1.7	49	1.7	49	0.013
K, mg L^{-1}	49	1.7	49	1.7	49	0.02
Mg, mg L^{-1}	49	0.74	49	0.74	49	0.01
Mn, mg L^{-1}	44	11	20	2.7	48	0.04
Na, mg L^{-1}	49	0.90	49	0.90	49	0.02
NH_4^+, mg L^{-1}	49	4.1	26	2.0	49	0.06
NO_3^-, mg L^{-1}						
all batches	47	3.2	29	2.7	49	0.076
aliquot 3	10	3.6	4	0.62	11	0.072
aliquot 5	37	3.1	24	2.6	38	0.078
pH						
air-equilibrated	49	0.02	--	--	--	--
initial ANC	49	0.03	--	--	--	--
initial BNC	49	0.07	--	--	--	--
P, total, mg L^{-1}						
all values	49	16	23	5.4	49	0.011
$\bar{x}$ <= 0.010	24	22	0	--		
$\bar{x}$ > 0.010	25	5.5	23	5.4		
SiO_2, mg L^{-1}	49	3.1	49	3.1	49	0.12
SO_4^{2-}, mg L^{-1}	49	0.96	49	0.96	49	0.19

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE D-2. GLOBAL ANALYTICAL WITHIN-BATCH PRECISION

	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
Parameter	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
all values	19	31	8	42	19	0.013
$\bar{x}$ <= 0.010	11	19	0	--		
x > 0.010	8	42	8	42		
Al, total, mg L^{-1}						
all values	18	39	11	10	19	0.011
$\bar{x}$ <= 0.010	7	61	0	--		
$\bar{x}$ > 0.010	11	10	11	10		
ANC, μeq L^{-1}	18	67	--	--	--	--
Ca, mg L^{-1}	15	1.0	15	1.0	19	0.06
Cl^-, mg L^{-1}	19	56	16	4.4	19	0.06
Conductance, μS cm^{-1}	17	11	16	1.2	19	0.8
DIC, mg L^{-1}						
air-equilibrated	18	17	16	4.0	19	0.37
initial	19	6.7	19	6.7	19	0.37
DOC, mg L^{-1}						
all values	18	16	18	16	19	0.0
$\bar{x}$ <= 5	11	20	11	20		
$\bar{x}$ > 5	7	4.5	7	4.5		
Fe, mg L^{-1}	14	38	11	5.3	19	0.06
F^-, total dissolved, mg L^{-1}	19	3.3	16	3.6	19	0.002
K, mg L^{-1}	17	49	14	1.2	19	0.02
Mg, mg L^{-1}	13	0.78	13	0.78	19	0.00
Mn, mg L^{-1}	13	39	13	39	19	0.00
Na, mg L^{-1}	15	37	13	0.41	19	0.04
NH_4^+, mg L^{-1}	15	13	13	14	19	0.02
NO_3^-, mg L^{-1}						
all batches	16	36	15	3.7	19	0.080
aliquot 3	12	41	12	41	15	0.000
aliquot 5	4	4.5	4	4.5	4	0.035
pH						
air-equilibrated	19	0.03	0	--	--	--
initial ANC	19	0.06	0	--	--	--
initial BNC	19	0.08	0	--	--	--
P, total, mg L^{-1}						
all values	18	4.7	14	4.1	19	0.006
$\bar{x}$ <= 0.010	5	6.8	1	8.3		
$\bar{x}$ > 0.010	13	3.6	13	3.6		
SiO_2, mg L^{-1}	19	3.6	19	3.6	19	0.02
SO_4^{2-}, mg L^{-1}	19	11	16	2.2	19	0.05

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE D-3. USGS ANALYTICAL WITHIN-BATCH PRECISION

Parameter	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
Al, extractable, mg L^{-1}						
all values	7	7.5	4	3.9	10	0.019
$\bar{x} <= 0.010$	1	16	0	--		
$x > 0.010$	6	4.9	4	3.9		
Al, total, mg L^{-1}						
all values	10	4.5	10	4.5	10	0.004
$\bar{x} <= 0.010$	0	--	0	--		
$\bar{x} > 0.010$	10	4.5	10	4.5		
ANC, µeq L^{-1}	3	5.9	--	--	--	--
Ca, mg L^{-1}	10	0.66	10	0.66	10	0.00
Cl^-, mg L^{-1}	10	2.6	10	2.6	10	0.11
Conductance, µS cm^{-1}	10	0.51	10	0.51	10	1.1
DIC, mg L^{-1}						
air-equilibrated	10	3.6	7	3.9	10	0.41
initial	10	2.1	10	2.1	10	0.26
DOC, mg L^{-1}						
all values	10	10	8	1.7	10	1.4
$\bar{x} <= 5$	6	12	4	1.9		
$\bar{x} > 5$	4	0.89	4	0.89		
Fe, mg L^{-1}	10	2.1	10	2.1	10	0.02
F^-, total dissolved, mg L^{-1}	10	2.9	10	2.9	10	0.012
K, mg L^{-1}	10	0.91	10	0.91	10	0.00
Mg, mg L^{-1}	10	0.33	10	0.33	10	0.00
Mn, mg L^{-1}	10	0.73	10	0.73	10	0.02
Na, mg L^{-1}	10	1.6	10	1.6	10	0.00
NH_4^+, mg L^{-1}	10	3.7	10	3.7	10	0.03
NO_3^-, mg L^{-1}						
all batches	10	1.4	9	1.5	10	0.013
aliquot 3	10	1.4	9	1.5	10	0.013
aliquot 5	0	--	0	--	0	--
pH						
air-equilibrated	10	0.26	--	--	--	--
initial ANC	10	0.10	--	--	--	--
initial BNC	10	0.13	--	--	--	--
P, total, mg L^{-1}						
all values	9	3.0	9	3.0	10	0.000
$\bar{x} <= 0.010$	0	--	0	--		
$\bar{x} > 0.010$	9	3.0	9	3.0		
SiO_2, mg L^{-1}	10	0.87	10	0.87	10	0.04
SO_4^{2-}, mg L^{-1}	10	1.3	10	1.3	10	0.27

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

TABLE D-4. VERSAR ANALYTICAL WITHIN-BATCH PRECISION

Parameter	Pairs with Mean > 0		Pairs with Mean > $10s_B$		Quantitation Limit	
	n	RMS of %RSD[a]	n	RMS of %RSD[a]	n	$10s_B$
Al, total extractable, mg L^{-1}						
all values	48	4.2	7	2.9	49	0.053
$\bar{x}$ <= 0.010	4	3.7	0	--		
x > 0.010	44	4.2	7	2.9		
Al, total, mg L^{-1}						
all values	49	6.6	49	6.6	49	0.013
$\bar{x}$ <= 0.010	0	--	0	--		
$\bar{x}$ > 0.010		6.6	49	6.6		
ANC, μeq L^{-1}	48	16	--	--	--	--
Ca, mg L^{-1}	49	0.55	49	0.55	49	0.02
Cl^-, mg L^{-1}	49	3.1	48	3.1	49	0.16
Conductance, μS cm^{-1}	49	17	48	17	49	1.3
DIC, mg L^{-1}						
air-equilibrated	49	1.6	49	1.6	48	0.15
initial	49	1.7	49	1.7	48	0.15
DOC, mg L^{-1}						
all values	49	2.5	44	2.6	49	1.0
$\bar{x}$ <= 5	43	2.5	38	2.6		
$\bar{x}$ > 5	6	2.5	6	2.5		
Fe, mg L^{-1}	49	2.9	49	2.9	49	0.01
F^-, total dissolved, mg L^{-1}	49	2.8	49	2.8	49	0.012
K, mg L^{-1}	49	1.4	49	1.4	49	0.06
Mg, mg L^{-1}	49	0.52	49	0.52	49	0.01
Mn, mg L^{-1}	35	24	35	24	49	0.01
Na, mg L^{-1}	49	0.94	49	0.94	49	0.15
NH_4^+, mg L^{-1}	47	7.3	18	1.9	49	0.21
NO_3^-, mg L^{-1}						
all batches	49	4.8	39	4.2	47	0.233
aliquot 3	19	5.0	17	4.8	17	0.177
aliquot 5	30	2.4	23	4.0	30	0.261
pH						
air-equilibrated	49	0.02	--	--	--	--
initial ANC	49	0.01	--	--	--	--
initial BNC	49	0.02	--	--	--	--
P, total, mg L^{-1}						
all values	49	13	49	13	49	0.005
$\bar{x}$ <= 0.010	1	0.00	1	0.00		
$\bar{x}$ > 0.010	48	13	48	13		
SiO_2, mg L^{-1}	49	1.4	21	1.5	49	3.56
SO_4^{2-}, mg L^{-1}	49	17	49	17	49	0.18

[a] Root mean square of percent relative standard deviation (RMS of absolute SD for pH).

APPENDIX E

OVERALL AND ANALYTICAL AMONG-BATCH PRECISION BY LABORATORY FOR 23 PARAMETERS, EASTERN LAKE SURVEY - PHASE I

Values were estimated from field natural, Lot 2 (FN2) and field natural, Lot 3 (FN3) audit sampled data, field and laboratory high synthetic (FH, LH) audit sample data, and field and laboratory low synthetic (FL and LL) audit sample data.

TABLE E-1. EMSI OVERALL AMONG-BATCH PRECISION

Parameter	FN2 Samples (n = 18) Mean	FN2 Samples (n = 18) %RSD[a]	FN3 Samples (n = 3) Mean	FN3 Samples (n = 3) %RSD[a]
Al, mg L^{-1}				
total extractable	0.175	25	0.002[b]	143
total	0.357	16	0.032[b]	125
ANC, µeq L^{-1}	4.3[b]	74	841.0	1.0
Ca, mg L^{-1}	1.87	7.9	57.84[c]	135[c]
Cl^-, mg L^{-1}	0.51	2.0	1.40	1.4
Conductance, µS cm^{-1}	26.7	3.1	97.4	1.1
DIC, mg L^{-1}				
air-equilibrated	0.17[b]	52	9.61	4.4
initial	0.39[b]	16	9.86	4.2
DOC, mg L^{-1}	3.2	4.3	1.5[b]	10
Fe, mg L^{-1}	0.02[b]	75	0.00[b]	--
F^-, total dissolved, mg L^{-1}	0.076	2.6	0.035	2.0
K, mg L^{-1}	0.49	4.6	0.52	3.5
Mg, mg L^{-1}	0.34	1.9	2.74	1.5
Mn, mg L^{-1}	0.07	6.4	0.00[b]	--
Na, mg L^{-1}	0.68	2.6	1.34	3.2
NH_4^+, mg L^{-1}	0.07[b]	12	0.01[b]	201
NO_3^-, mg L^{-1}	1.449	2.6	1.46	3.3
pH				
air-equilibrated	5.25	0.40	8.18	0.10
initial ANC	5.07	0.03	7.86	0.08
initial BNC	5.11	0.05	7.88	0.06
P, total, mg L^{-1}	0.001	158	0.001	187
SiO_2, mg L^{-1}	4.36	4.0	2.66	3.7
SO_4^{2-}, mg L^{-1}	6.89	2.1	3.32	0.83

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with mean equal to zero.,

[b] Mean less than quantitation limit (see Table C-1).

[c] When one confirmed but questionable value of 147.7 mg L^{-1} is omitted, mean = 12.91 mg L^{-1} and RSD = 5.7 percent.

TABLE E-2. GLOBAL OVERALL AMONG-BATCH PRECISION[a]

Parameter	FN2 Samples (n = 3) Mean	 %RSD[b]
Al, mg L^{-1}		
total extractable	0.112	59
total	0.242	7.9
ANC, µeq L^{-1}	5.5[c]	85
Ca, mg L^{-1}	1.81	3.1
Cl^-, mg L^{-1}	0.52	2.2
Conductance, µS cm^{-1}	25.6	3.5
DIC, mg L^{-1}		
air-equilibrated	0.39[c]	80
initial	0.68[c]	19
DOC, mg L^{-1}	3.4	11
Fe, mg L^{-1}	0.01[c]	173
F^-, total dissolved, mg L^{-1}	0.079	5.5
K, mg L^{-1}	0.49	2.0
Mg, mg L^{-1}	0.34	1.7
Mn, mg L^{-1}	0.10[c]	64
Na, mg L^{-1}	0.69	0.83
NH_4^+, mg L^{-1}	0.09[c]	43
NO_3^-, mg L^{-1}	1.471	2.5
pH		
air-equilibrated	5.14	0.03
initial ANC	5.13	0.02
initial BNC	5.11	0.02
P, total, mg L^{-1}	0.001[c]	284
SiO_2, mg L^{-1}	4.88	5.3
SO_4^{2-}, mg L^{-1}	6.72	1.8

[a] No FN3 samples were analyzed by Global.

[b] Relative standard deviation (absolute SD for pH).

[c] Mean less than quantitation limit (see Table C-2).

TABLE E-3. USGS OVERALL AMONG-BATCH PRECISION[a]

	FN2 Samples (n = 3)	
Parameter	Mean	%RSD[b]
Al, mg L^{-1}		
total extractable	0.165	11
total	0.166[c]	70
ANC, µeq L^{-1}	-3.4[c]	395
Ca, mg L^{-1}	2.36	13
Cl^-, mg L^{-1}	0.83	51
Conductance, µS cm^{-1}	28.6	6.8
DIC, mg L^{-1}		
air-equilibrated	0.26[c]	38
initial	0.23[c]	37
DOC, mg L^{-1}	3.7	25
Fe, mg L^{-1}	0.01	7.7
F^-, total dissolved, mg L^{-1}	0.077	6.6
K, mg L^{-1}	0.49	1.1
Mg, mg L^{-1}	0.35	2.1
Mn, mg L^{-1}	0.07	0.81
Na, mg L^{-1}	0.71	4.7
NH_4^+, mg L^{-1}	0.07	50
NO_3^-, mg L^{-1}	1.457	3.1
pH		
air-equilibrated	5.10	0.05
initial ANC	5.04	0.05
initial BNC	5.06	0.01
P, total, mg L^{-1}	0.003[c]	96
SiO_2, mg L^{-1}	4.27	0.66
SO_4^{2-}, mg L^{-1}	7.27	9.7

[a] No FN3 samples were analyzed by USGS.

[b] Percent relative standard deviation (absolute SD for pH).

[c] Mean less than quantitation limit (see Table C-3).

TABLE E-4. VERSAR OVERALL AMONG-BATCH PRECISION

	FN2 Samples (n = 17)		FN3 Samples (n = 4)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable	0.205	35	0.002[b]	43
total	0.286	25	0.014[b]	86
ANC, μeq L^{-1}	0.8[b]	797	853.7	3.0
Ca, mg L^{-1}	1.89	1.2	13.10	3.2
Cl$^-$, mg L^{-1}	0.69	6.3	1.38	2.3
Conductance, μS cm^{-1}	26.5	0.74	95.7	1.8
DIC, mg L^{-1}				
air-equilibrated	0.17[b]	24	9.74	3.8
initial	0.45[b]	14	9.99	4.7
DOC, mg L^{-1}	3.16	6.4	1.3[b]	6.3
Fe, mg L^{-1}	0.02[b]	33	0.00[b]	--
F$^-$, total dissolved, mg L^{-1}	0.078	4.2	0.035[b]	6.9
K, mg L^{-1}	0.48 [b]	4.6	0.47[b]	16
Mg, mg L^{-1}	0.35	1.9	2.84	4.1
Mn, mg L^{-1}	0.06	7.7	0.01	200
Na, mg L^{-1}	0.66	6.6	1.28	7.9
NH$_4^+$, mg L^{-1}	0.04[b]	93	0.01[b]	68
NO$_3^-$, mg L^{-1}	1.386[b]	7.4	1.363[b]	5.3
pH				
air-equilibrated	5.13	0.04	8.26	0.05
initial ANC	5.05	0.05	7.68	0.09
initial BNC	5.05	0.03	7.72	0.10
P, total, mg L^{-1}	0.002[b]	127	0.002[b]	122
SiO$_2$, mg L^{-1}	4.22	10	2.78[b]	7.2
SO$_4^{2-}$, mg L^{-1}	6.99	10	3.22	4.0

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with mean equal to zero.

[b] Mean equal to or less than quantitation limit (see Table C-4).

TABLE E-5. EMSI OVERALL AND ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FH Samples (n = 14)		LH Samples (n = 9)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, $mg\ L^{-1}$				
total extractable[b]	--	--	0.153	20
total	0.233	23	0.219	35
ANC, $\mu eq\ L^{-1}$	465.8	23	483.9	19
Ca, $mg\ L^{-1}$				
Lot 4 (n = 11, 9)	1.65	9.3	1.50	14
Lots 5 and 6 (n = 3, 0)	1.73	3.3	--	--
Cl^-, $mg\ L^{-1}$				
Lot 4 (n = 6, 9)	3.33	3.0	3.36	1.5
Lots 5 and 6 (n = 3, 0)	4.03	1.1	--	--
Conductance, $\mu S\ cm^{-1}$	103.3	1.4	102.3	2.1
DIC, $mg\ L^{-1}$				
air-equilibrated	4.79	32	4.99	33
initial	7.43	28	7.26	27
DOC, $mg\ L^{-1}$	9.8	24	10.4	20
Fe, $mg\ L^{-1}$[b]	--	--	0.18	11
F^-, total dissolved, $mg\ L^{-1}$	0.438	5.5	0.439	2.9
K, $mg\ L^{-1}$	3.07	2.5	3.08	2.4
Mg, $mg\ L^{-1}$	2.32	1.8	2.33	2.1
Mn, $mg\ L^{-1}$	1.13	16	1.38	3.2
Na, $mg\ L^{-1}$	11.83	8.6	11.67	9.9
NH_4^+, $mg\ L^{-1}$	1.25	16	1.35	9.1
NO_3^-, $mg\ L^{-1}$	1.661	29	1.353	45
pH				
air-equilibrated	7.62	0.58	7.81	0.14
initial ANC	6.96	0.25	6.94	0.30
initial BNC	7.00	0.26	7.06	0.31
P, total, $mg\ L^{-1}$	0.054	16	0.062	4.3
SiO_2, $mg\ L^{-1}$	9.01	14	9.08	15
SO_4^{2-}, $mg\ L^{-1}$	14.6	2.1	14.73	2.4

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$.

[b] Laboratory synthetic audit samples only (see Section 4).

TABLE E-6. GLOBAL AND ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FH Samples (n = 5)		LH Samples (n = 2)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.129	21
total	0.175	6.3	0.177	0.80
ANC, μeq L^{-1}	482.7	15	392.1	49
Ca, mg L^{-1}				
Lot 4 (n = 3, 1)	1.69	2.4	1.65	--
Lots 5 and 6 (n = 2, 1)	1.90	4.1	1.82	--
Cl$^-$, mg L^{-1}				
Lot 4 (n = 3, 1)	3.15	1.8	3.27	--
Lots 5 and 6 (n = 2, 1)	4.10	5.7	3.95	--
Conductance, μS cm^{-1}	100.5	4.5	103.1	3.9
DIC, mg L^{-1}				
air-equilibrated	4.94	26	5.97	9.4
initial	5.26	18	6.46	3.7
DOC, mg L^{-1}	10.8	20	9.9	4.3
Fe, mg L^{-1}[b]	--	--	0.18	7.9
F$^-$, total dissolved, mg L^{-1}	0.440	3.2	0.430	2.3
K, mg L^{-1}	3.08	4.5	2.97	3.6
Mg, mg L^{-1}	2.27	2.9	2.24	3.8
Mn, mg L^{-1}	1.17	18	1.44	2.0
Na, mg L^{-1}	12.04	14	13.07	2.8
NH_4^+, mg L^{-1}	1.23	10	1.27	0.17
NO_3^-, mg L^{-1}	1.313	60	1.464	15
pH				
air-equilibrated	7.89	0.08	7.94	0.05
initial ANC	7.15	0.22	7.00	0.01
initial BNC	7.10	0.25	7.04	0.05
P, total, mg L^{-1}	0.048	19	0.054	9.3
SiO_2, mg L^{-1}	10.13	13	11.55	4.0
SO_4^{2-}, mg L^{-1}	13.96	2.8	14.65	0.77

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X}$ = 0 or where n = 1.

[b] Laboratory synthetic audit samples only (see Section 4).

TABLE E-7. USGS OVERALL AND ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FH Samples (n = 3)		LH Samples (n = 1)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.159	--
total	0.175[c]	3.2	0.175	--
ANC, μeq L^{-1}	542.7	2.8	554.7	--
Ca, mg L^{-1}				
Lot 4 (n = 0, 0)	--	--	--	--
Lots 5 and 6 (n = 3, 1)	2.00	13	1.81	--
Cl^-, mg L^{-1}				
Lot 4 (n = 0, 0)	--	--	--	--
Lots 5 and 6 (n = 3, 1)	3.50	17	2.96	--
Conductance, μS cm^{-1}	110.6	1.4	111.1	--
DIC, mg L^{-1}				
air-equilibrated	6.33	13	6.01	--
initial	6.55	26	6.03	--
DOC, mg L^{-1}	10.0	18	10.1	--
Fe, mg L^{-1}[b]	--	--	0.12	--
F^-, total dissolved, mg L^{-1}	0.455	0.46	0.456	--
K, mg L^{-1}	3.11	4.9	3.10	--
Mg, mg L^{-1}	2.33	2.8	2.28	--
Mn, mg L^{-1}	1.32	6.4	1.47	--
Na, mg L^{-1}	12.47	0.90	12.34	--
NH_4^+, mg L^{-1}	1.32	10	1.42	--
NO_3^-, mg L^{-1}	1.700	29	2.02	--
pH				
air-equilibrated	7.71	0.06	7.65	--
initial ANC	7.29	0.35	7.38	--
initial BNC	7.53	0.24	7.38	--
P, total, mg L^{-1}	0.061	23	0.075	--
SiO_2, mg L^{-1}	10.07	1.6	10.24	--
SO_4^{2-}, mg L^{-1}	14.53	3.2	14.10	--

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$ or where n = 1.

[b] Laboratory synthetic audit samples only (see Section 4).

[c] Mean less than quantitation limit (see Table C-3).

TABLE E-8. VERSAR OVERALL ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FH Samples (n = 14)		LH Samples (n = 9)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.177	12
total	0.179	37	0.176	37
ANC, µeq L^{-1}	471.4	13	502.5	16
Ca, mg L^{-1}				
Lot 4 (n = 6, 4)	1.68	2.2	1.65	2.0
Lots 5 and 6 (n = 8, 5)	2.03	2.1	2.02	1.0
Cl^-, mg L^{-1}				
Lot 4 (n = 6, 4)	4.52	57	3.49	13
Lots 5 and 6 (n = 8, 5)	4.15	23	6.75	92
Conductance, µS cm^{-1}	105.9	4.2	105.7	4.5
DIC, mg L^{-1}				
air-equilibrated	4.22	18	4.19	17
initial	4.57	21	4.50	20
DOC, mg L^{-1}	9.9	16	10.2	16
Fe, mg L^{-1}[b]	--	--	0.18	6.3
F^-, total dissolved, mg L^{-1}	0.451	14	0.430	2.4
K, mg L^{-1}	2.96	9.2	2.96	6.4
Mg, mg L^{-1}	2.45	2.2	2.43	1.9
Mn, mg L^{-1}	1.23	6.0	1.38	1.9
Na, mg L^{-1}	11.64	7.5	11.76	8.1
NH_4^+, mg L^{-1}	1.26	12	1.35	18
NO_3^-, mg L^{-1}	1.800	21	1.57	44
pH				
air-equilibrated	7.75	0.64	7.95	0.13
initial ANC	7.14	0.20	7.14	0.20
initial BNC	7.16	0.21	7.14	0.21
P, total, mg L^{-1}	0.062	26	0.060	22
SiO_2, mg L^{-1}	8.94	14	9.20	14
SO_4^{2-}, mg L^{-1}	14.32	8.4	14.20	6.5

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$.

[b] Laboratory synthetic audit samples only (see Section 4).

TABLE E-9. EMSI OVERALL ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FL Samples (n = 16)		LL Samples (n = 16)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.017	34
total	0.025[b]	16	0.033	54
ANC, µeq L^{-1}	112.8	6.1	115	6.8
Ca, mg L^{-1}				
Lot 4 (n = 11, 10)	0.14	8.4	0.13	9.9
Lots 5 and 6 (n = 5, 6)	0.17	3.6	0.17	9.5
Cl^-, mg L^{-1}				
Lot 4 (n = 11, 10)	0.39[c]	87	0.29	7.3
Lots 5 and 6 (n = 5, 6)	0.32[c]	2.6	0.31	1.7
Conductance, µS cm^{-1}	18.9	7.9	18.5	5.4
DIC, mg L^{-1}				
air-equilibrated	1.34	8.2	1.32	8.5
initial	1.83	7.2	1.75	15
DOC, mg L^{-1}	0.9[c]	45	1.28	78
Fe, mg L^{-1}[b]	--	--	0.08	21
F^-, total dissolved, mg L^{-1}	0.041	24	0.040	6.8
K, mg L^{-1}	0.22	11	0.22	10
Mg, mg L^{-1}	0.41	8.8	0.42	2.9
Mn, mg L^{-1}	0.09	7.0	0.10	6.3
Na, mg L^{-1}	2.75	3.9	2.77	3.4
NH_4^+, mg L^{-1}	0.18[c]	23	0.20	17
NO_3^-, mg L^{-1}	0.547	8.3	0.609	60
pH				
air-equilibrated	7.24	0.05	7.23	0.05
initial ANC	6.83	0.07	6.82	0.09
initial BNC	6.93	0.13	6.90	0.12
P, total, mg L^{-1}	0.022	35	0.021	24
SiO_2, mg L^{-1}	1.00	43	0.97	16
SO_4^{2-}, mg L^{-1}	2.38	9.8	2.30	1.8

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$.

[b] Laboratory synthetic audit samples only (see Section 4).

[c] Mean less than quantitation limit (see Table C-1).

TABLE E-10. GLOBAL OVERALL ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FL Samples (n = 7)		LL Samples (n = 8)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.015	33
total	0.020[c]	38	0.019	38
ANC, µeq L^{-1}	115.13	6.2	115.15	6.4
Ca, mg L^{-1}				
Lot 4 (n = 1, 2)	0.16[c]	--	0.17	4.3
Lots 5 and 6 (n = 6, 6)	0.17[c]	4.4	0.16	9.9
Cl^-, mg L^{-1}				
Lot 4 (n = 1, 2)	0.26	--	0.30	2.4
Lots 5 and 6 (n = 6, 6)	0.33	8.4	0.33	7.9
Conductance, µS cm^{-1}	18.0	7.1	17.8	8.0
DIC, mg L^{-1}				
air-equilibrated	1.37	13	1.35	19
initial	1.66	12	1.75	15
DOC, mg L^{-1}	1.3[c]	57	1.5	50
Fe, mg L^{-1}[b]	--	--	0.06[d]	40
F^-, total dissolved, mg L^{-1}	0.041	5.9	0.040	5.4
K, mg L^{-1}	0.23	12	0.24	10
Mg, mg L^{-1}	0.42	10	0.42	8.2
Mn, mg L^{-1}	0.09	19	0.10	6.3
Na, mg L^{-1}	2.66	1.7	2.51	19
NH_4^+, mg L^{-1}	0.15	20	0.16	11
NO_3^-, mg L^{-1}	0.245	105	0.29	92
pH				
air-equilibrated	7.40	0.02	7.40	0.02
initial ANC	6.96	0.10	6.99	0.11
initial BNC	7.00	0.13	7.00	0.12
P, total, mg L^{-1}	0.019[c]	35	0.024	82
SiO_2, mg L^{-1}	1.29	9.1	1.26	11
SO_4^{2-}, mg L^{-1}	2.21	3.3	2.21	2.5

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X}$ = 0 or where n = 1.

[b] Laboratory synthetic audit samples only (see Section 4).

[c] Mean less than quantitation limit (see Table C-2).

[d] Mean equal to or less than quantitation limit (see Table D-2).

TABLE E-11. USGS OVERALL ANALYTICAL AMONG-BATCH PRECISION

Parameter	Overall Among-Batch Precision FL Samples (n = 4)		Analytical Among-Batch Precision LL Samples (n = 3)	
	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.014[d]	28
total	0.018[c]	12	0.080	120
ANC, μeq L^{-1}	112.6	14	106.5	2.9
Ca, mg L^{-1}				
Lot 4 (n = 0, 0)	--	--	--	--
Lots 5 and 6 (n = 4, 3)	0.17	10	0.17	8.6
Cl^-, mg L^{-1}				
Lot 4 (n = 0, 0)	--	--	--	--
Lots 5 and 6 (n = 4, 3)	0.40	24	0.33	12
Conductance, μS cm^{-1}	21.1	1.6	20.8	1.2
DIC, mg L^{-1}				
air-equilibrated	1.41	7.7	1.44	8.3
initial	1.44	1.9	1.43	14
DOC, mg L^{-1}	1.2	49	1.3[c]	7.1
Fe, mg L^{-1}[b]	--	--	0.05	12
F^-, total dissolved, mg L^{-1}	0.040	1.3	0.040	1.4
K, mg L^{-1}	0.32	27	0.23	13
Mg, mg L^{-1}	0.43	3.3	0.43	4.0
Mn, mg L^{-1}	0.09	1.6	0.10	2.8
Na, mg L^{-1}	2.76	2.1	2.75	2.7
NH_4^+, mg L^{-1}	0.16	8.9	0.17	8.5
NO_3^-, mg L^{-1}	0.267	108	0.355	81
pH				
air-equilibrated	7.25	0.15	7.08	0.07
initial ANC	6.93	0.12	6.80	0.14
initial BNC	7.22	0.50	7.11	0.33
P, total, mg L^{-1}	0.020	19	0.022	24
SiO_2, mg L^{-1}	1.03	1.1	1.04	2.4
SO_4^{2-}, mg L^{-1}	2.23	4.8	2.23	4.1

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$.

[b] Laboratory synthetic audit samples only (see Section 4).

[c] Mean equal to or less than quantitation limit (see Table C-3).

[d] Mean less than quantitation limit (see Table D-3).

TABLE E-12. VERSAR OVERALL ANALYTICAL AMONG-BATCH PRECISION

	Overall Among-Batch Precision		Analytical Among-Batch Precision	
	FL Samples (n = 16)		LL Samples (n = 16)	
Parameter	Mean	%RSD[a]	Mean	%RSD[a]
Al, mg L^{-1}				
total extractable[b]	--	--	0.022[d]	17
total	0.025[c]	20	0.027	32
ANC, μeq L^{-1}	108.9	7.0	103.2	11
Ca, mg L^{-1}				
Lot 4 (n = 11, 11)	0.15[c]	24	0.14	5.3
Lots 5 and 6 (n = 5, 5)	0.16[c]	5.7	0.15	2.9
Cl^-, mg L^{-1}				
Lot 4 (n = 11, 11)	0.28[c]	11	0.31	18
Lots 5 and 6 (n = 5, 5)	0.43	26	0.42	51
Conductance, μS cm^{-1}	19.0	3.8	18.9	3.8
DIC, mg L^{-1}				
air-equilibrated	1.35	9.3	1.36	9.0
initial	1.52	8.9	1.54	8.7
DOC, mg L^{-1}	0.9[c]	41	0.9	30
Fe, mg L^{-1}[b]	--	--	0.07	10
F^-, total dissolved, mg L^{-1}	0.044	24	0.04	5.0
K, mg L^{-1}	0.22	9.3	0.22	9.1
Mg, mg L^{-1}	0.44	2.3	0.44	1.8
Mn, mg L^{-1}	0.09	5.8	0.08	24
Na, mg L^{-1}	2.68	7.1	2.68	6.2
NH_4^+, mg L^{-1}	0.14[c]	36	0.19[d]	28
NO_3^-, mg L^{-1}	0.458[c]	32	0.481	18
pH				
air-equilibrated	7.43	0.16	7.33	0.15
initial ANC	6.85	0.12	6.85	0.12
initial BNC	6.91	0.09	6.89	0.11
P, total, mg L^{-1}	0.020[c]	25	0.022	22
SiO_2, mg L^{-1}	0.87[c]	21	0.94	22
SO_4^{2-}, mg L^{-1}	2.21[c]	12	2.32	5.9

[a] Percent relative standard deviation (absolute SD for pH). Not applicable for pairs with $\overline{X} = 0$.

[b] Laboratory synthetic audit samples only (see Section 4).

[c] Mean equal to or less than quantitation limit (see Table C-4).

[d] Mean less than quantitation limit (see Table D-4).